LARGE-SCALE MERCURY CONTROL TECHNOLOGY TESTING FOR LIGNITE-FIRED UTILITIES – OXIDATION SYSTEMS FOR WET FGD

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ABSTRACT

The Energy & Environmental Research Center (EERC) is conducting a consortium-based effort directed toward resolving the mercury control issues facing the lignite industry. Specifically, the EERC team—the EERC, the Electric Power Research Institute (EPRI), URS Corporation (URS), ADA-ES, the Babcock & Wilcox Company, the North Dakota Industrial Commission, SaskPower, and the Mercury Task Force, which includes Basin Electric Power Cooperative, Otter Tail Power Company, Great River Energy, TXU Energy (TXU), Montana–Dakota Utilities Co., Minnkota Power Cooperative, BNI Coal, Ltd., Dakota Westmoreland Corporation, and North American Coal Corporation—has undertaken a project to significantly and cost-effectively oxidize elemental mercury (Hg) in lignite combustion gases, followed by capture in a wet scrubber. The applicability of this approach is expected to increase because of an expected demand for scrubbed systems in lignite utilities as well as subbituminous utilities in the United States and Canada. The oxidation process is proven at the pilot scale and in short-term full-scale tests. Additional optimization is continuing on oxidation technologies, and this project focuses on monthlong full-scale testing.

The lignite industry has been proactive in advancing the understanding of, and identifying control options for, Hg in lignite combustion flue gases. Approximately 3 years ago, the EERC and EPRI began a series of Hg-related discussions with the Mercury Task Force as well as utilities firing Texas and Saskatchewan lignites. This project is one of three being undertaken by the consortium to perform large-scale Hg control technology testing to address the specific needs and challenges to be met in controlling Hg from lignite-fired power plants.

This project involves Hg oxidation upstream of a system equipped with an electrostatic precipitator (ESP) followed by wet flue gas desulfurization (FGD). The team involved in conducting the technical aspects of the project includes the EERC, Babcock & Wilcox, EPRI, URS, and ADA-ES. The host sites include Minnkota Power Cooperative Milton R. Young (MRY) Station Unit 2 and TXU Monticello Steam Electric Unit 3. The work involves establishing Hg oxidation levels upstream of air pollution control devices (APCDs) and removal rates across existing ESP and FGD units, determining costs associated with those removal rates, investigating the possibility of the APCD acting as a multipollutant control device, quantifying the balance-of-plant impacts of the control technologies, and facilitating technology commercialization.

MRY Plant

In the previous reporting period, the preliminary results of field testing were reported. During this reporting period, the baseline corrosion probes were characterized to determine if any increased corrosion.

Monticello Plant

Field testing was initiated at the Monticello site, and testing will be completed in the next reporting period.

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NOMENCLATURE

AHI	air heater inlet
AHO	air heater outlet
APCD	air pollution control device
B&W	Babcock & Wilcox Company
BOP	balance of plant
CMM	continuous mercury monitor
DOE	U.S. Department of Energy
ECM	economizer
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
FF	fabric filter
FGD	flue gas desulfurization
Hg^0	elemental mercury
Hg^{2+}	mercuric compounds
$HgCl_2$	mercuric chloride
ICR	Information Collection Request (EPA)
MRY	Milton R. Young Station
NDIC	North Dakota Industrial Commission
NETL	National Energy Technology Laboratory
OH	Ontario Hydro
PAC	powdered activated carbon
pc	pulverized coal
QA	quality assurance
QC	quality control
SCA	specific collection area
SDA	spray dryer absorber
SEA	sorbent enhancement additive
SEM	scanning electron microscopy
SOA	solid oxidizing additive
TXU	TXU Energy
URS	URS Corporation

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The other projects cover sorbent injection technologies for systems equipped with ESPs and those equipped with spray dryer absorbers combined with fabric filters (SDA–FF) and an alternative oxidation technology. The intent of the proposed testing is to help maintain the viability of lignite-fired energy production by providing utilities with lower-cost options for meeting future Hg regulations.

2.0 BACKGROUND

Mercury is an immediate concern for the U.S. electric power industry because of the U.S. Environmental Protection Agency (EPA) December 2000 decision that regulation of Hg from coal-fired electric utility plants is appropriate and necessary under Section 112 of the Clean Air Act (1). EPA determined that Hg emissions from power plants pose significant hazards to public health and must be reduced. The EPA *Mercury Study Report to Congress* (2) and the *Utility Hazardous Air Pollutant Report to Congress* (3) identified coal-fired boilers as the largest single source of atmospheric Hg emissions in the United States, accounting for about one-third of the total anthropogenic emissions. On December 15, 2003, EPA published the proposed Utility Mercury Reductions Rule in order to solicit comments on multiple approaches for mercury emission control. EPA reviewed comments on the proposed rule and put forth regulations in March 2005.

Even though Hg regulations for coal-fired utilities are imminent, significant issues remain and need to be resolved. The U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) has acknowledged that data gaps exist for Hg control technologies for the immense U.S. reserves of lignite and subbituminous coals. The primary challenge is that these coals produce flue gases in which difficult-to-control Hg^0 is the dominant form. The EPA Information Collection Request (ICR) indicates that questions still exist regarding the impact of various APCDs and technologies for lignite-fired units on their ability to control Hg^0 emissions. The lignite-based consortium believes that there is a critical need for large-scale Hg oxidation testing at lignite-fired power plants equipped with an ESP and wet FGD. This project has been developed based on the input of consortium members and DOE guidance to address these issues.

In general, lignitic coals are unique because of their highly variable ash content, which is rich in alkali and alkaline-earth elements and has high oxygen and moisture levels and low chlorine content. Lignite coals typically contain comparable levels of Hg but significantly lower levels of chlorine compared to bituminous coals. Lignites have chlorine concentrations well below 200 ppm in the coal, whereas Appalachian and Illinois Basin bituminous coals can have chlorine levels in excess of 1000 ppm. These differences in composition have important effects on the form of Hg emitted from a boiler and the capabilities of different control technologies to remove Hg from flue gas. Coals containing chlorine levels greater than 200 ppm typically produce flue gas dominated by more easily removable mercuric compounds (Hg^{2+}), most likely mercuric chloride ($HgCl_2$). Conversely, experimental results indicate that low-chlorine (<50 ppm) coal combustion flue gases (typical of lignite) contain predominantly Hg^0, which is substantially more difficult to remove than Hg^{2+} (3). Additionally, the generally high alkali and alkaline-earth content of lignite coals may reduce the oxidizing effect of the already-low chlorine content by reactively scavenging chlorine species (Cl, HCl, and Cl_2) from the combustion flue gas. The level of chlorine in flue gases of recently tested lignites from North Dakota and Saskatchewan ranged from 2.6 to 3.4 ppmv, with chlorine content ranging from 11 to 18 ppmw in the coal on a dry basis, respectively.

Few published data exist that demonstrate the effectiveness of oxidation technologies for plants firing lignite coal. Lignite-fired power plants have shown a limited ability to control Hg emissions in currently installed ESPs, SDAs, and wet FGD systems (4). This low level of control

can be attributed to the high proportions of Hg^0 present in the flue gas. Typically, in the pulverized coal (pc)- and cyclone-fired units, the Hg^0 content is greater than 85% of the total; the average emitted from North Dakota lignite-fired power plants is roughly 6.3 lb/TBtu (4, 5). Figure 1 shows resulting Hg emissions measured using the Ontario Hydro (OH) method and continuous mercury monitors (CMMs) at the furnace exit during pilot tests at the EERC with North Dakota lignite. These results are consistent with the ICR results discussed above and with the recent baseline data for the proposed test sites, as shown later.

The mercury oxidation technologies being investigated for lignites include catalysts and chemical agents. The catalysts that have been tested include selective catalytic reduction catalysts for NO_x reduction, noble metal-impregnated catalysts, and oxide-impregnated catalysts. The chemical agents include chlorine-containing salts (chloride compounds) and cofiring fuels that contain oxidizing agents (6, 7).

Theoretically, the use of chloride compounds to oxidize Hg^0 to Hg^{2+} makes sense. The evidence includes chemical kinetic modeling of bench-scale test results, indicating that the introduction of chloride compounds into the high-temperature furnace region will likely result in the production of atomic chlorine and/or molecular chlorine, which are generally thought to be the dominant Hg^0 reactants in coal combustion flue gases (6). The formation of atomic chlorine is a key pathway involved in the chemical reaction mechanisms that result in the oxidation of Hg^0 (6). The pathway for Hg oxidation is gas-phase Hg^0 oxidation by atomic chlorine (chlorine radical). Recent kinetic modeling of chlorine radical formation as a function of temperature

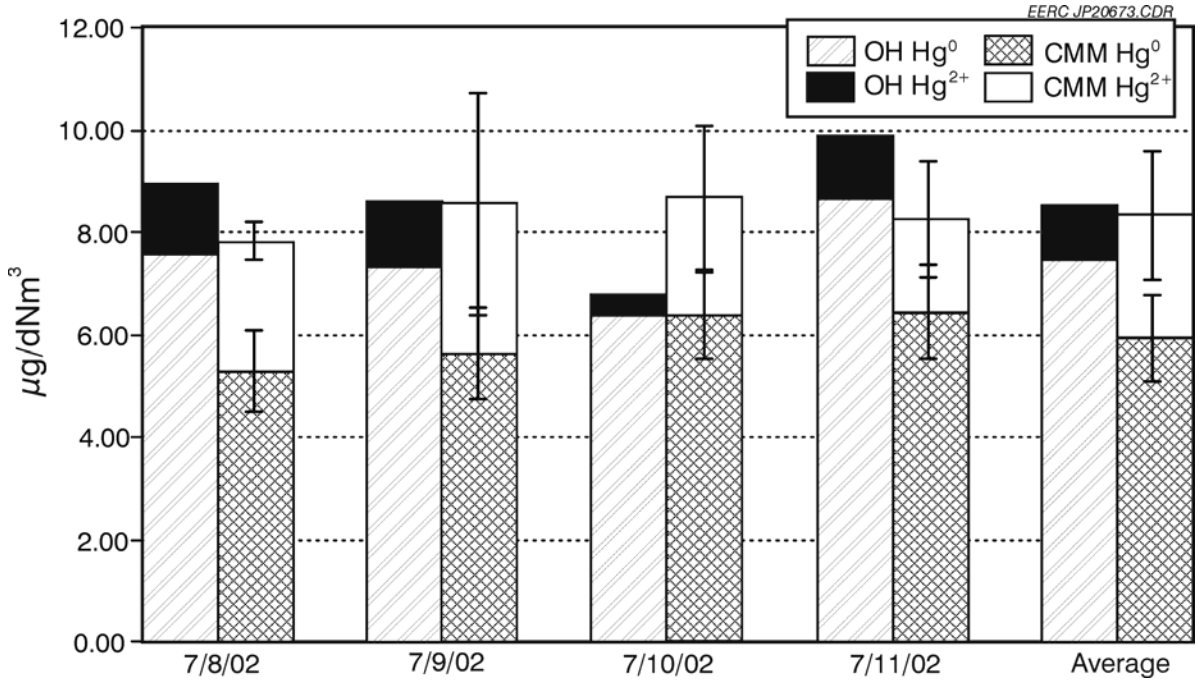

Figure 1. Inlet mercury speciation for Freedom, North Dakota, lignite (µg/dNm^3 = microgram per dry normal cubic meter [corrected to 0°C and 3% O_2]).

and residence time is shown in Figure 2. The results indicate the importance of temperature in the abundance of chlorine radicals. Recent work, supported by EPRI, indicated that the injection of HCl in lower-temperature regions downstream of the boiler was ineffective in oxidizing Hg^0, while the injection of salt into the furnace resulted in significant oxidation (8).

Fuel additives for Hg oxidation have recently been tested in a pilot-scale system. Chemical additives or oxidants such as chloride salts have shown the ability to convert Hg^0 to more reactive oxidized forms, as shown in Figure 3. In addition, recent EPRI short-term testing conducted at a 70-MW_e pc-fired North Dakota power plant indicated that the injection of chloride salts can result in increased Hg oxidation in the flue gas (8). Hg oxidation of up to 70% was observed at a salt injection rate that resulted in an HCl concentration of 110 ppm in the flue gas, as shown in Figure 4. In addition, the injection of salt resulted in the enhanced removal of Hg across the SDA–FF, with removal efficiencies of up to 50% in short-term field testing (8).

Because of the promise seen in the oxidation of Hg in flue gases produced from lignite coals, the project team is conducting long-term field testing of Hg oxidation and removal using a wet FGD at MRY Unit 2 and Monticello Unit 3.

MRY Unit 2 is a B&W Carolina-type radiant boiler designed to burn high-moisture, high-slagging/fouling North Dakota lignite. Nominally rated at 3,050,000 lb/hr, this unit is a cyclone-fired, balanced-draft, pump-assisted circulation boiler. The unit began commercial operation in May 1977 and is base-loaded at 450 MW gross. The unit is equipped with a cold-side ESP for particulate control and a wet FGD unit for SO_2 control. The cold-side ESP has a specific

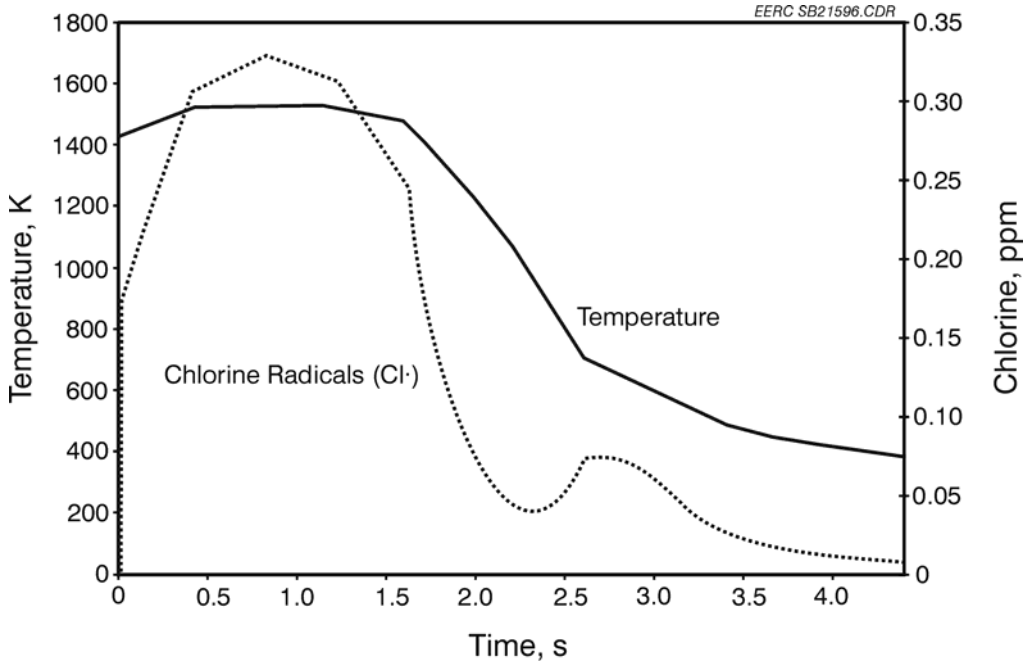

Figure 2. Prediction of chlorine radical formation as a function of temperature and residence time typical of a utility boiler using a kinetic model (Chemkin).

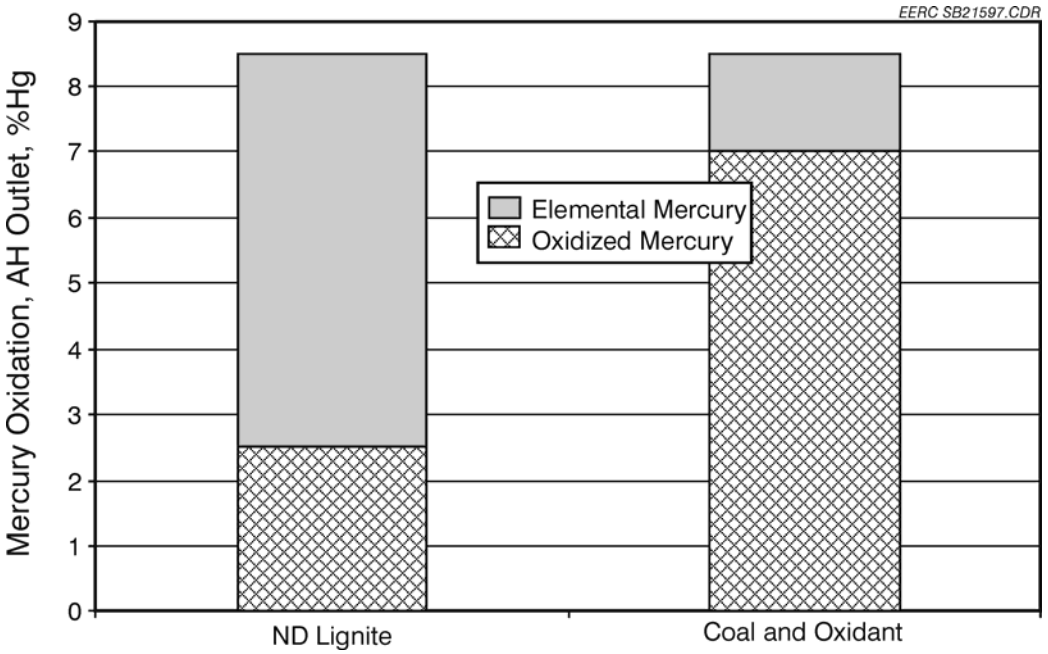

Figure 3. Oxidation of mercury through the addition of a chlorine-containing additive to the coal in EERC pilot-scale testing.

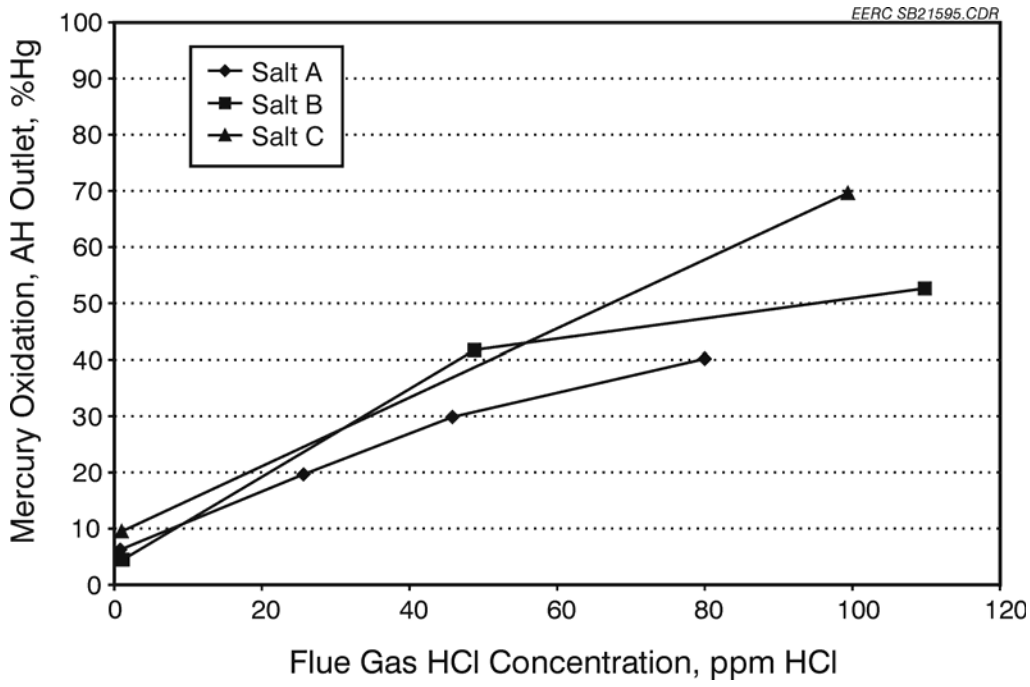

Figure 4. Comparison of mercury oxidation and HCl flue gas content for a range of salt injections at a North Dakota lignite-fired power plant (8).

collection area (SCA) of 375 ft^2/1000 acfm. The wet FGD for SO_2 control utilizes alkaline ash and lime. The MRY Plant fires North Dakota lignite coal from the Kinneman Creek and Hagel seams at the Center Mine. This plant and configuration are ideal for testing Hg oxidation and control in a wet scrubber. The high-temperature environment in the cyclone will easily vaporize and transform the chlorine species into highly reactive radical forms. The system has been tested for Hg speciation and control.

Flue gas sampling for speciated Hg was conducted on MRY Unit 2 at the ESP inlet, FGD inlet, and stack from October 22 through November 14, 2002. The sampling was carried out using both the OH method and CMMs (9). A schematic of the plant and sample locations is in Figure 5. The sampling involved the OH method at the ESP inlet, FGD inlet, and stack. In addition to OH method sampling, two CMMs, one at the FGD inlet and one at the stack, were used to monitor speciated Hg levels. The CMMs were operated to obtain 20 days of data at the two locations.

The average Hg speciation results from Unit 2 OH method flue gas sampling are summarized in Figure 6A. The average Hg emissions at the stack were 95% Hg^0. Two CMMs were operated at the FGD inlet and stack locations of Unit 2 to gather Hg variability data. Statistical analysis of the CMM data indicates that the average Hg concentration was 10.7 ± 2.7 µg/m^3 (90th percentile) at the FGD inlet and 9.3 ± 2.2 µg/m^3 at the stack. Hg-level fluctuations resulting from minor coal changes as well as other variability in plant operations were found to fall within 24% of the average. A Hg balance for MRY Unit 2 (10) was determined by comparing the rate of Hg entering the plant to the rate of Hg leaving the plant. The resulting material balances ranged from 102% to 103%.

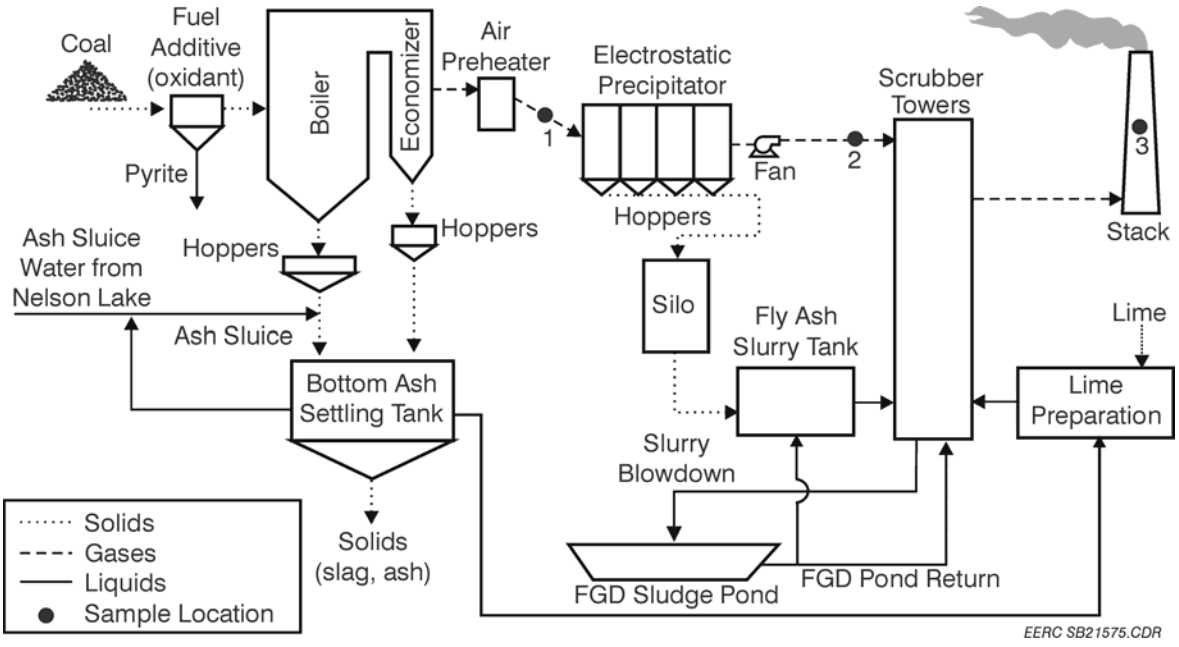

Figure 5. Schematic for MRY Unit 2 showing sampling locations.

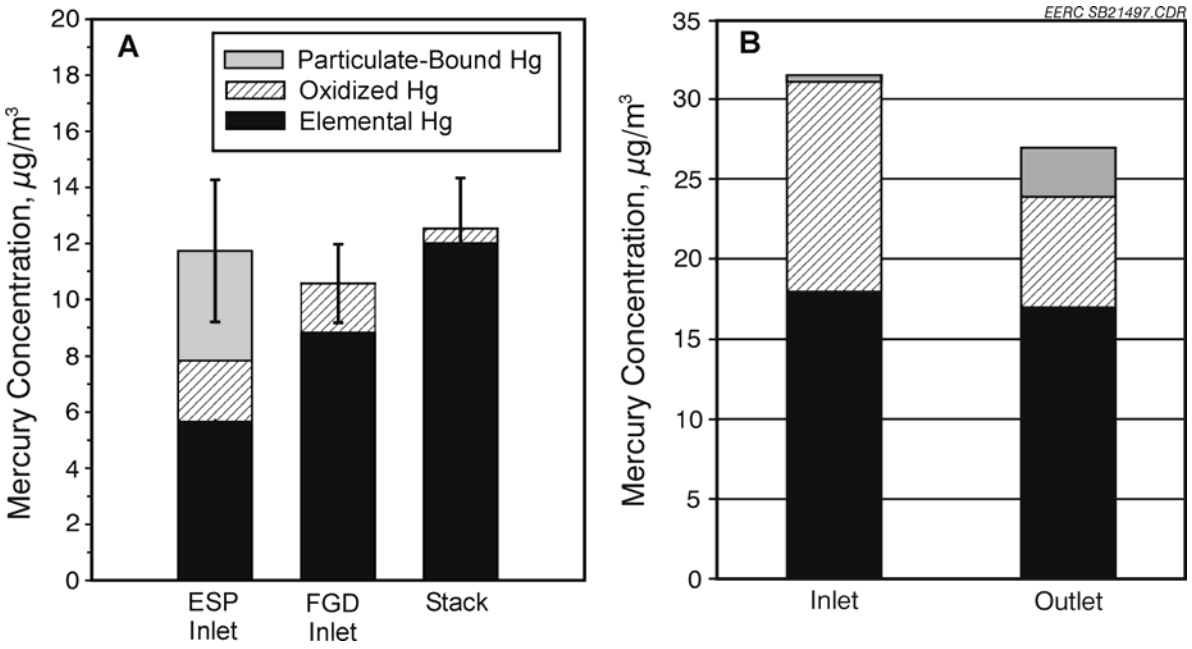

Figure 6. A) MRY OH mercury data obtained in October–November 2002 and B) OH mercury data for Monticello (ICR data).

The second site is TXU Monticello Unit 3 located near Mt. Pleasant, Texas. This site is also well characterized for Hg speciation, emissions, and variability. In addition, it provides an opportunity to test the Hg oxidation technology on a Texas lignite. Figure 7 illustrates the Unit 3 gas path. Unit 3 has a 750-MW B&W wall-fired, Carolina-type universal pressure boiler that fires Texas lignite coal from the upper and lower Wilcox seam. The unit was placed in commercial operation in 1978 and fires 640 tons/hr of Texas lignite at full-rated load. Downstream of the air preheater, the gas flows through a cold-side ESP constructed by Hamon Research-Cottrell, Inc. The ESP has ten fields with a SCA of 900 ft^2/1000 acfm. The ESP outlet temperature is nominally 300°F.

The results of Hg speciation measurements at the inlet and outlet of the scrubbers at Monticello Unit 3 are shown in Figure 6B. The results of the OH method sampling indicate that 57% of the total Hg is in the elemental form entering the wet FGD and that the Hg^0 is not captured with the wet FGD. Results from the ICR tests at Monticello Unit 3 suggest approximately 15% Hg removal across the FGD system, which is consistent with the trends for other units firing low-rank lignite coals.

3.0 EXPERIMENTAL

3.1 Objectives

The objective of this project is to demonstrate the effectiveness of chemical addition for reducing Hg emissions from flue gas derived from lignite. Full-scale tests will be performed at

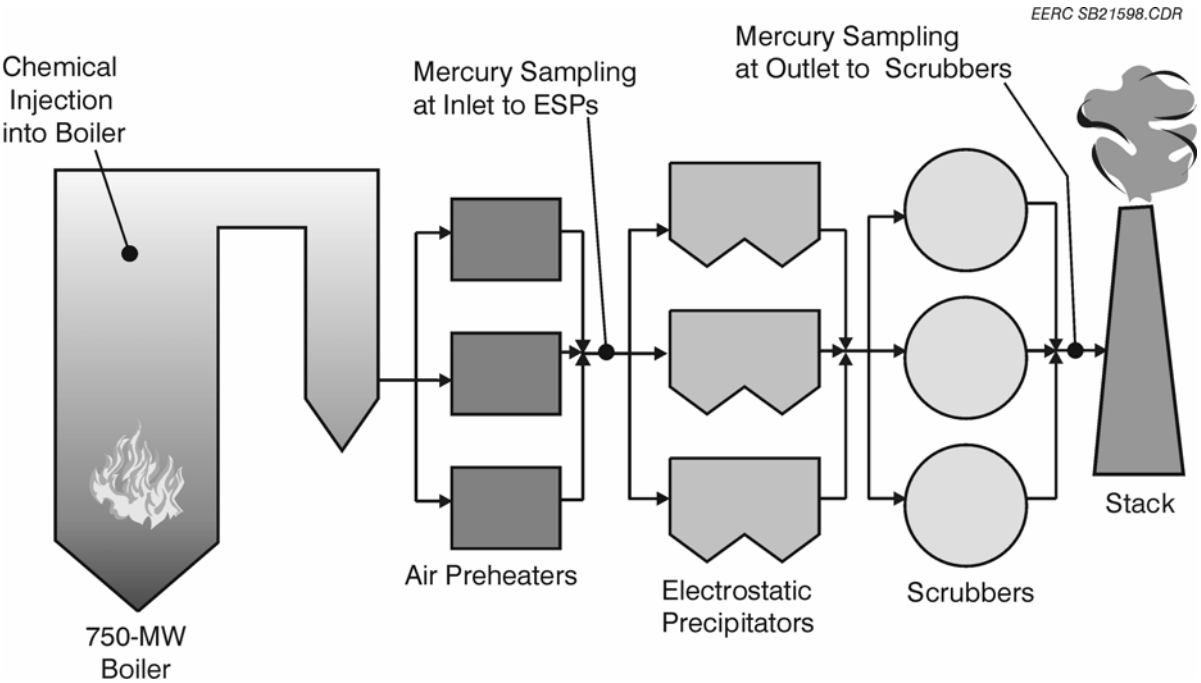

Figure 7. Plant schematic for Monticello Unit 3.

MRY Unit 2 and Monticello Unit 3 to evaluate chemical addition performance across an ESP wet scrubber configuration.

The objective of MRY Unit 2 testing is to determine the impact of chemical addition on Hg speciation, overall Hg removal from the flue gas using the combination of the ESP and wet scrubber, and the impact of the additive salts on corrosion and deposition on system components. The objective of Monticello Unit 3 testing is to provide additional data on Hg oxidation and removal efficiency when a lignite coal from Texas is fired. Data from this program will be used to perform an economic analysis of the costs associated with full-scale implementation of a chemical addition system.

3.2 Planned Scope of Work

The scope of work includes testing oxidation technology for controlling Hg emissions at two lignite-fired power plants equipped with wet FGD systems. The plants include MRY Unit 2 (cyclone-fired, North Dakota lignite, ESP, wet FGD) and Monticello Unit 3 (wall-fired, Texas lignite, ESP, wet FGD). The technology involves the injection of a chemical additive (sorbent enhancement additive [SEA]) with the lignite or injection into the furnace to oxidize Hg upstream of a wet FGD system. The two plants with different firing systems and lignite types will be tested to determine the following: the degree of mercury oxidation as a function of chemical addition rate, Hg removal efficiencies, economics, and BOP impacts. The additive will be added at rates equivalent to 300–1000 ppm chlorine in the coal during parametric testing, with a target of less than 500 ppm in the coal for the long term if selected. A second additive (SEA2) has repeatedly been shown to be even more effective than chlorine and will therefore be tested,

as well. In addition, small amounts of solid oxidizing additive (SOA [activated carbon in this case]) will be added (<1 lb/Macf) to further enhance oxidation. The 2-month test will be conducted using the additive that performs the best during parametric testing. If fractions of lb/Macf of carbon are shown effective in enhancing the SEA impact, it will also be considered for the 2-month test.

4.0 RESULTS AND DISCUSSION

4.1 Summary of Activities Conducted July – September 2005

4.1.1 MRY Plant

In the previous reporting period, a meeting on-site was conducted with MRY personnel, a detailed test plan was finalized, and corrosion probes were installed at the MRY plant November 18, 2004. During this reporting period, longer-term testing of the oxidizing agent along with a small amount of powdered activated carbon (PAC) was conducted. In addition, the baseline corrosion probes were removed and replaced with probes to be exposed during the 4-week test period. Mercury sampling and measurement were conducted using CMM and OH method sampling.

4.1.2 Monticello Plant

Planning is under way for testing at Monticello, which will follow the MRY tests. A draft of the testing plan was prepared and sent to project sponsors and participants for their review. A meeting between the EERC and URS was conducted to provide URS personnel an overview of the testing results obtained at the MRY plant.

4.2 Results from MRY Testing

The work conducted this quarter consisted of characterization of the corrosion probes. The results of the probe characterization are discussed in detail in Section 4.2.7. Sections 4.2.1 through 4.2.6 were conducted in prior quarters.

4.2.1 Installation of Oxidant and PAC Injection Systems

The oxidant or SEA injection system consists of liquid storage tanks, a metering and pumping skid, and injection lances. Three tanks for storage and diluting the solutions of SEA are shown in Figure 8. Each tank has a storage capacity of 3100 gallons. The SEA pumping and metering skid is shown in Figure 9. This system is capable of pumping the SEA solutions at rates of 0.1 to 2.2 gal/min. This allowed for the injection of SEA at rates up to 500 ppm on an as-fired coal basis. The SEA was injected into the coal pipes prior to being fed into the cyclones. The injection of SEA was conducted at four cyclones. The injection lances are shown in Figure 10.

Figure 8. Oxidant or SEA storage tanks at MRY.

Figure 9. SEA pumping and metering skid.

In addition to the SEA injection system, a PAC injection system was installed that allowed for the injection of a small amount of PAC upstream of the ESP. The PAC consisted of an Apogee portapac metering skid, blower, connecting lines, and injection lances. The injection of carbon was conducted at 16 locations into the ductwork upstream of the ESP, as shown in Figure 11. In addition, the location upstream of the ESP was also for OH method sampling and CMM. The other locations for mercury sampling and measurement were between the ESP and scrubber, as well as at the stack. The stack location is illustrated in Figure 12.

Figure 10. SEA injection lances shown installed at MRY.

Figure 11. PAC injection and OH and CMM sampling locations.

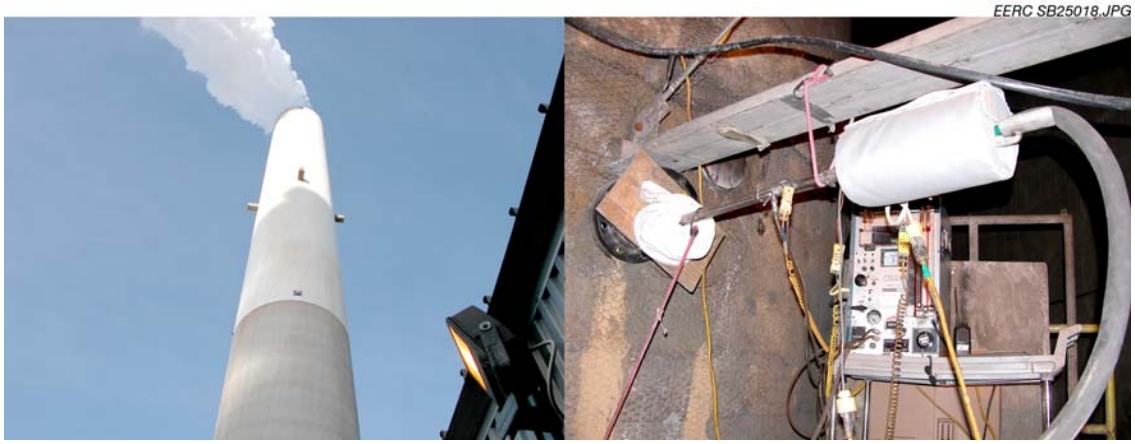

Figure 12. OH and CMM mercury-sampling and measurement location on the stack.

4.2.2 Baseline and Parametric Testing

The baseline and parametric testing was initiated with baseline testing on March 15 and completed in early April 2005. During the baseline testing, OH and CMM measurements were made. Following the baseline testing, three rates of PAC were tested to determine the removal with PAC alone. The next testing was conducted with SEA1 ($CaCl_2$) alone. This testing was followed by combining both SEA1 and PAC at three rates. In addition, a short test was conducted with $MgCl_2$ to determine the differences between the types of oxidant. SEA2 was injected following the testing of SEA1. SEA2 was injected at three rates and was combined with PAC. All of the data that will be presented are preliminary and have not gone through complete quality assurance/quality control (QA/QC). Not all the coal analyses and other data were available for interpreting the results presented in this report.

Baseline OH method testing is shown in Figure 13 for the three replicate tests. The baseline values at this time are preliminary and have not been compared to coal mercury levels. The results show that the total level of Hg at the inlet varies from about 12 to 16 µg/Nm^3. The speciation at the inlet does not represent forms of Hg in the flue gas stream because of the reaction of the dust cake formed on the filter with the gas-phase mercury. The measurements downstream of the ESP after the particulate materials have been removed are more representative of the mercury species present in the flue gas. The elemental form is the most abundant at the FGD inlet and at the stack. The results indicate very little removal across the ESP/FGD. The results shown in Figure 13A are typical of past testing results, as shown in Figure 6A.

4.2.3 Mercury Speciation with SEA and Carbon Addition

The aim of the project was to add components to the coal to enhance the formation of oxidized and particulate forms of mercury, thus enabling the capture of mercury in the ESP and wet FGD. The first SEA tested was $CaCl_2$. These injection rates are on a dry-coal basis. The mercury speciation in the flue gas derived from the combustion of Center lignite with the addition of $CaCl_2$ is shown in Figure 14. The results indicate that the abundance of oxidized and

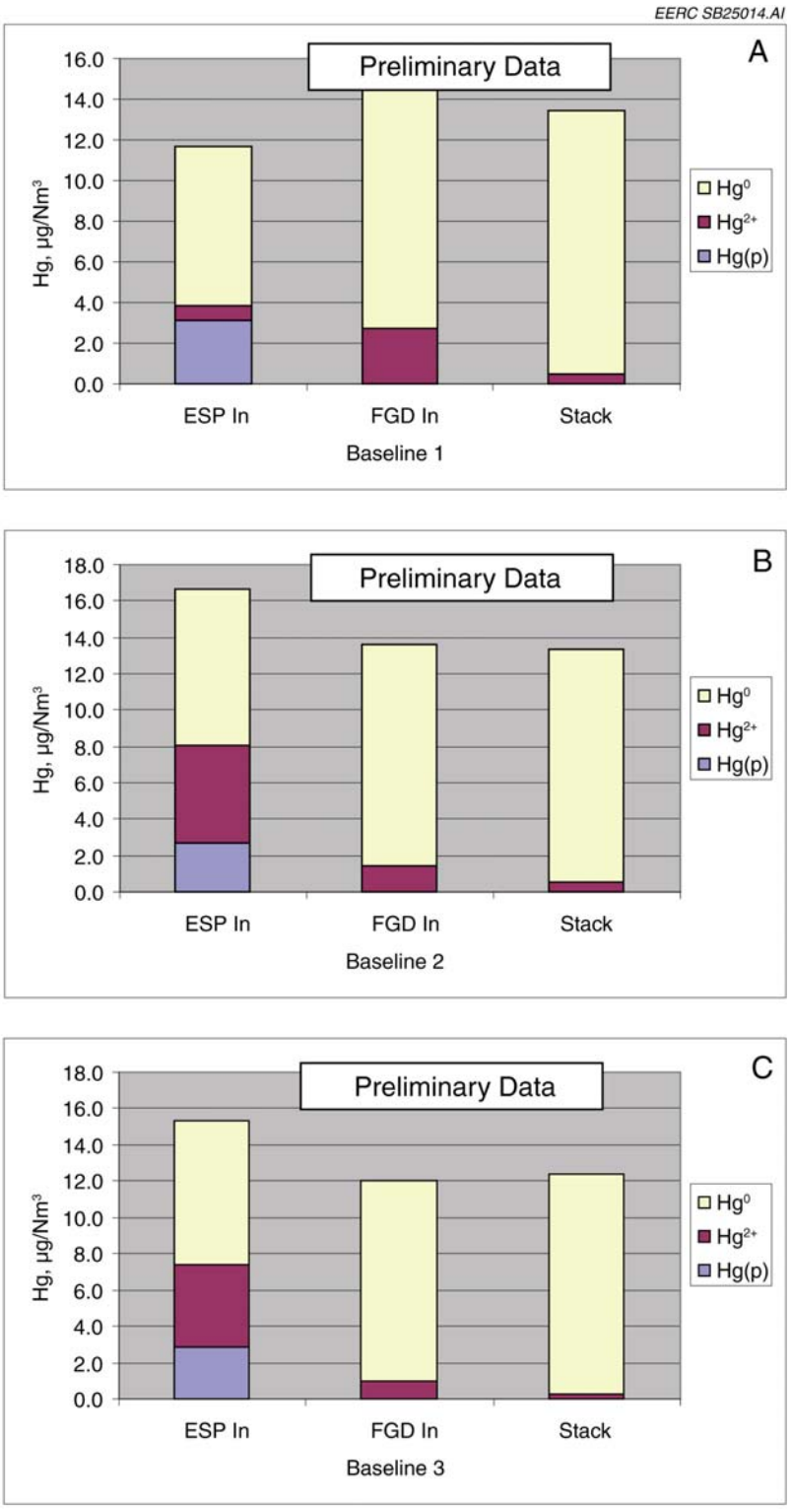

Figure 13. Preliminary baseline OH method measurements at the A) ESP inlet, B) FGD inlet, and C) stack.

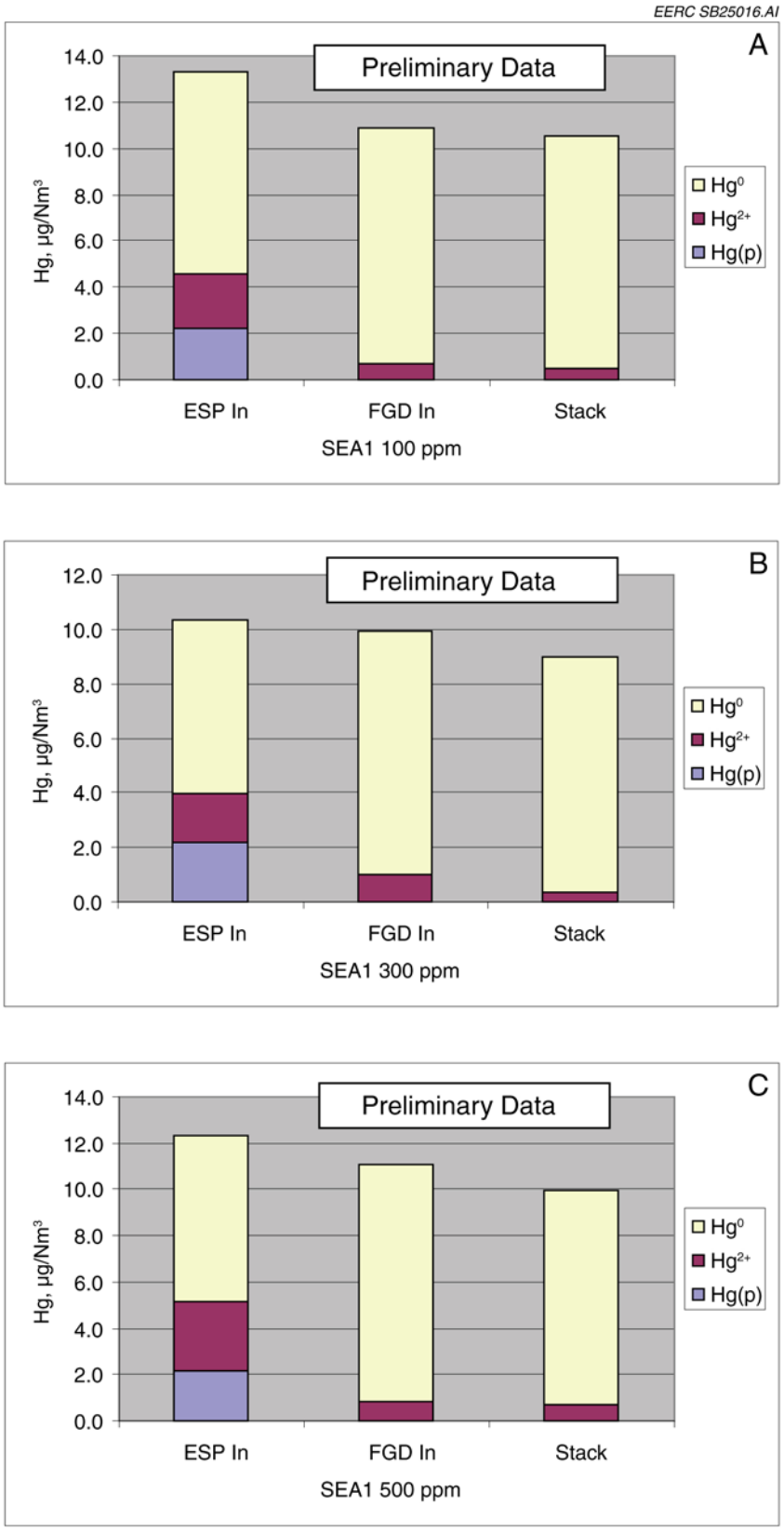

Figure 14. Mercury speciation with SEA1 added to coal.

particulate forms of mercury only increase slightly with the addition of $CaCl_2$ up to 500 ppm. These results differ significantly from the testing that was conducted in the EERC pilot-scale system where the degree of oxidation increased dramatically with the addition of $CaCl_2$ (11). The differences may be the result of the cyclone firing and the differences in coal characteristics. The cyclone firing will enhance the presence of alkali and alkaline-earth elements in the fly ash. In addition, the Center lignite fired during the testing has a high level of sodium. Sodium, along with calcium, has the potential to react with the chlorine and likely decrease its potential to react with elemental mercury.

Testing was also conducted using SEA2, which has shown significant promise in oxidizing Hg^0 and converting it into the particulate and oxidized forms. Figure 15 shows the forms of mercury and the levels of mercury at the ESP inlet, FGD inlet, and stack. The SEA2 significantly increases the level of particulate forms of mercury with only 25 ppm added on an as-fired-coal basis. The particulate and some of the oxidized forms of mercury are removed across the ESP. The remaining Hg^0 and Hg^{2+} were not removed by the FGD. Most of the removal occurred in the ESP.

4.2.4 Mercury Control with SEA Addition Only

The mercury removal attained with the addition of SEA1, SEA2, and $MgCl_2$ across both the ESP and FGD is shown in Figure 16. The $CaCl_2$ and $MgCl_2$ show similar results. The SEA2 shows appreciably higher removal rates with the addition of much smaller quantities. However, the goal of 55% removal was not achieved using up to 75 ppm addition of SEA_2. Surprisingly, nearly all of the mercury removal occurred in the ESP with little removal occurring in the FGD. It appears that what mercury is oxidized is removed in the ESP, with the remaining mercury in elemental form, which passes through the FGD. The SEA1 was not particularly effective in oxidizing and removing mercury, with stack CMM measurements indicating only 16% removal at 500 ppm SEA1 (ppm halogen on a dry-coal basis). The OH method measurements indicate a similar removal at the same SEA1 concentration based on stack OH method total mercury measurements relative to baseline.

The SEA2 shows appreciably higher removal rates with addition of much smaller quantities. However, the ability to achieve the goal of 55% removal was not achieved using up to 75 ppm addition of SEA2 which resulted in only 44% removal, as shown in Figure 17.

Although achieving higher mercury removal with smaller quantities of material, the behavior of the SEA2 is similar to that of SEA1 in that nearly all mercury removal occurred across the ESP, and the mercury exiting the ESP is primarily in elemental form.

4.2.5 Mercury Control with SEA and Carbon Injection

SEA with the addition of small amounts of carbon has been shown to enhance the oxidation of mercury as well as its capture (11). The results obtained at the MRY Station during parametric testing is shown in Figure 18. The results with PAC only show removals up to 35% with the addition of 1 lb/Macf. The addition of SEA1 showed some improvement at lower PAC

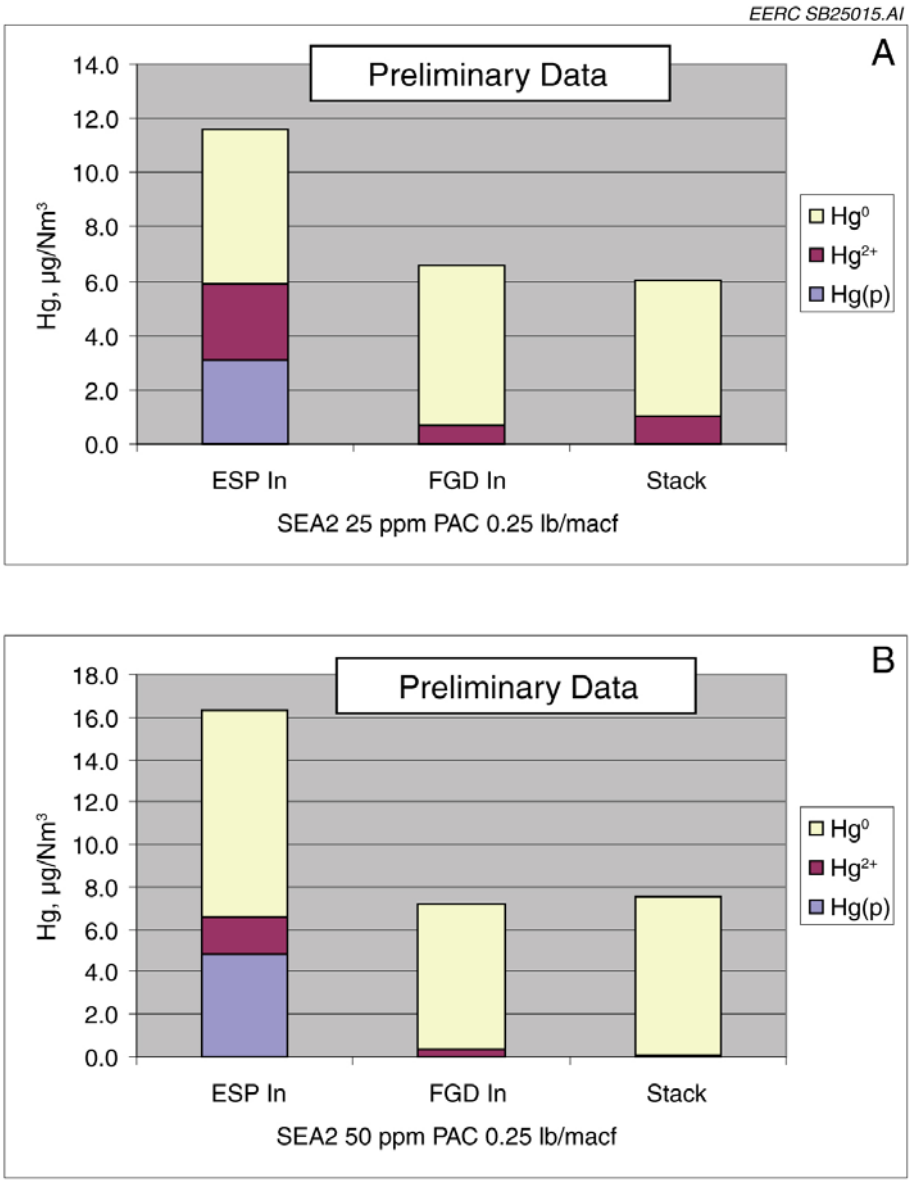

Figure 15. Mercury speciation with SEA2 and PAC addition.

addition rates, but showed no significant improvement at higher PAC addition rates. The improvement in capture using SEA1 with carbon was not as significant as the results obtained in other projects. The reason is likely the high sodium content and the ash partitioning during the cyclone combustion process. The results obtained with the combination of SEA2 and PAC showed much better removal than observed with SEA2 alone.

SEA1 in combination with PAC injection resulted in improved mercury removal as shown in Figure 19. At the highest rates tested of 300 ppm SEA1 with 1.00 lb/Macf PAC, the removal was 35% based on stack CMM measurements. However, this is significantly lower than the goal

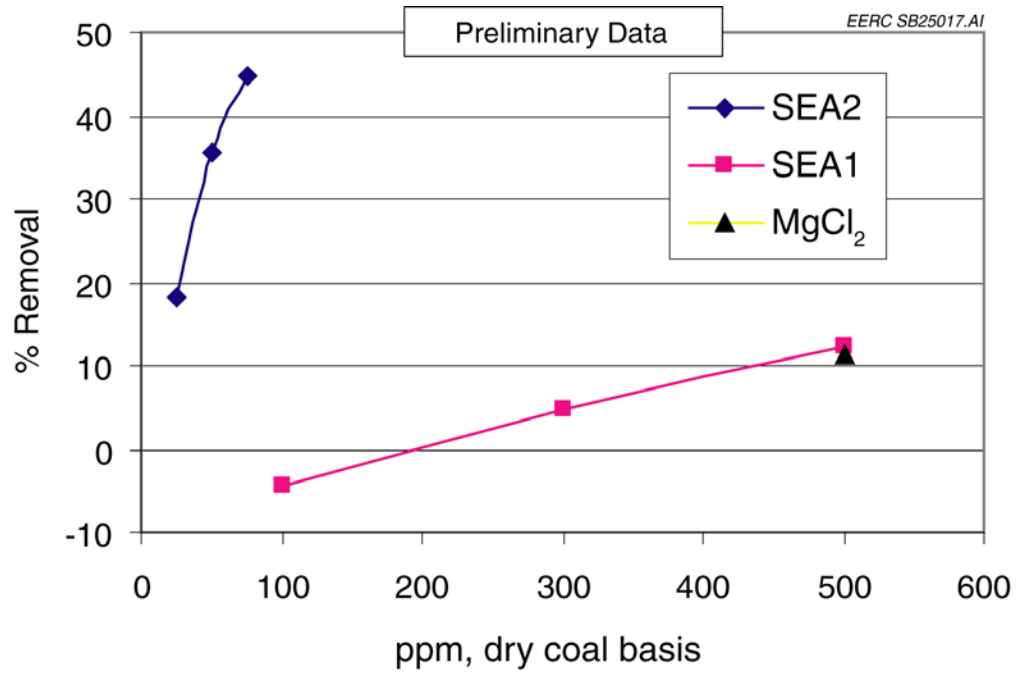

Figure 16. Mercury reduction across ESP and FGD using SEA only.

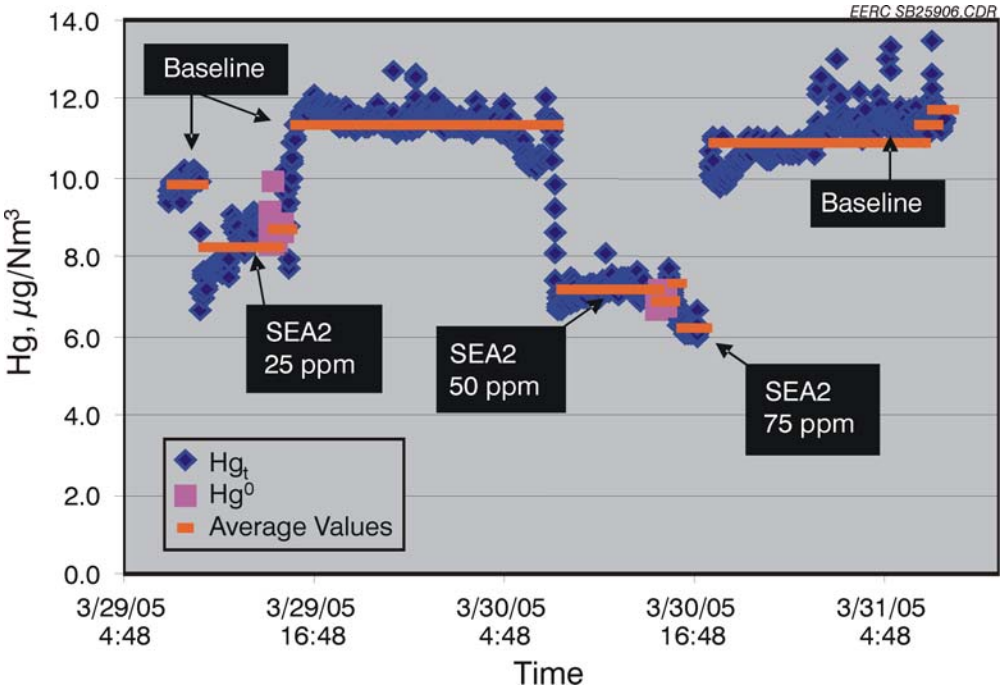

Figure 17. Mercury stack measurements conducted during the injection of SEA2.

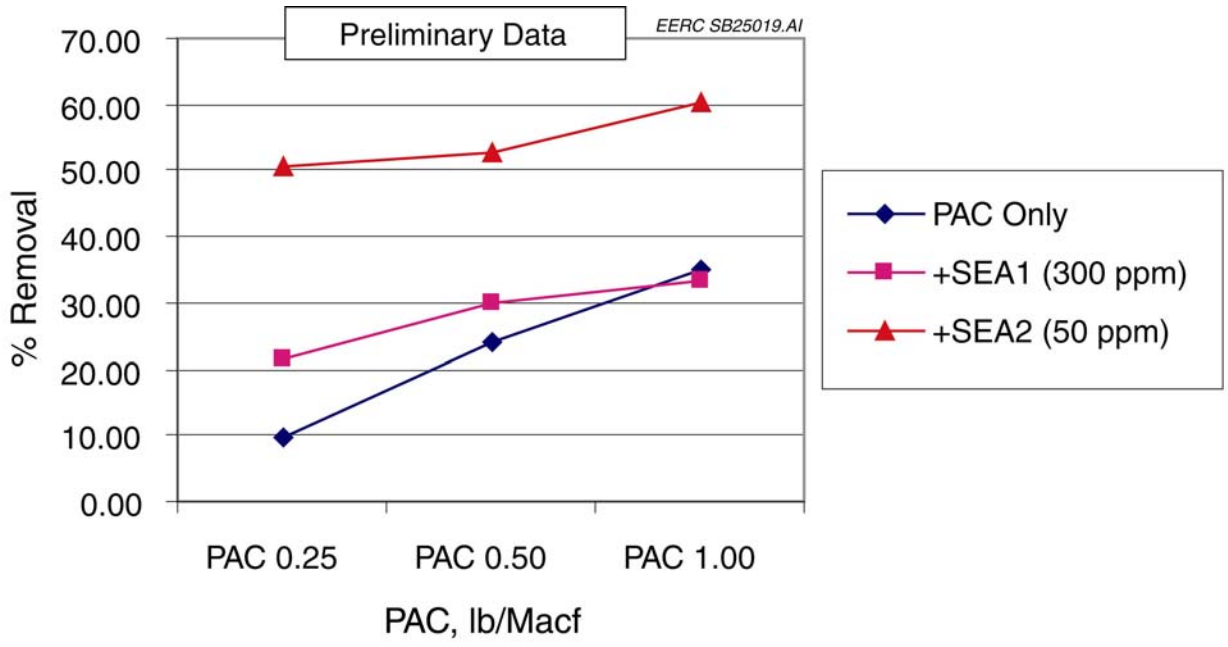

Figure 18. Mercury reduction with SEA or PAC.

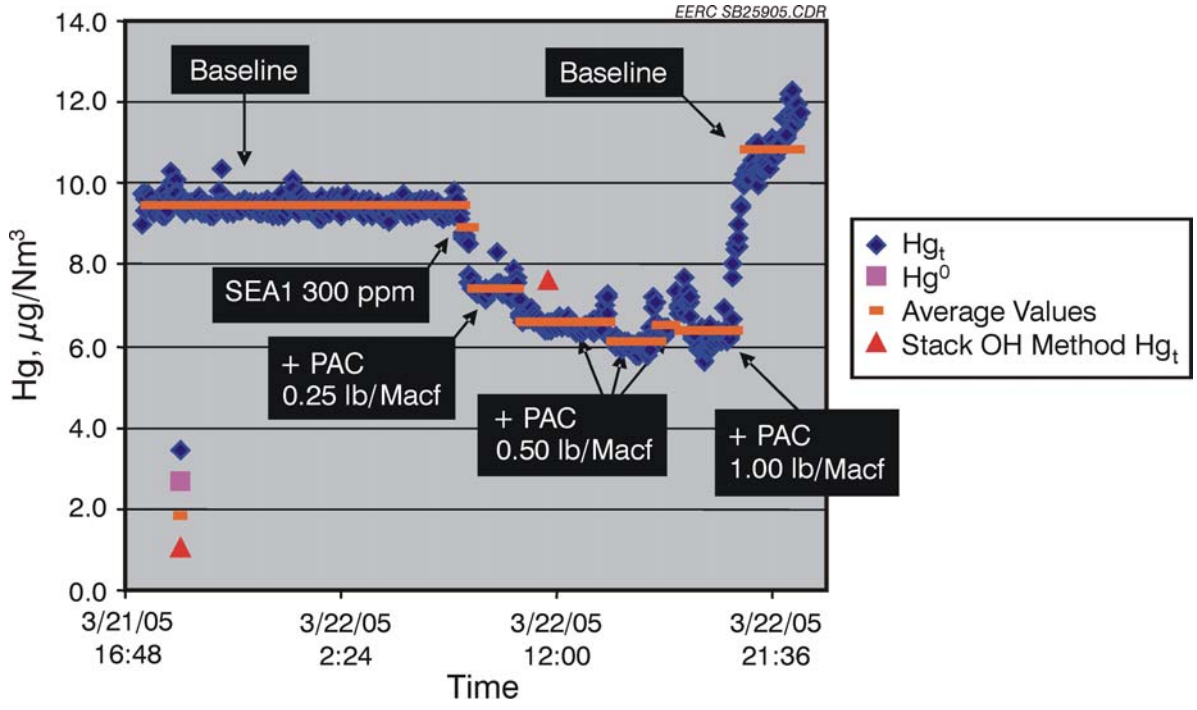

Figure 19. Mercury stack measurements during the injection of SEA1 and PAC.

of 55% removal. Again, nearly all of the mercury removal occurred across the ESP, with primarily Hg^0 exiting the ESP.

PAC alone performed nearly as well as when injected in combination with SEA1, achieving approximately 35% removal at a rate of 1.00 lb/Macf; at 1.80 lb/Macf, there was 53% mercury removal, which was near the 55% goal. The objectives of the project, however, precluded the use of PAC at such a high rate.

The results obtained at the MRY Station of SEA2 addition in combination with PAC injection are shown in Figure 20. These results, obtained with the combination of SEA2 and PAC, showed much better removal than observed with SEA2 alone. It was possible to obtain removals of 50% or better with 50 ppm SEA2 and 0.3–0.5 lb/Macf PAC.

4.2.6 Extended Testing at MRY

The objective of the extended testing was to demonstrate that approximately 55% mercury removal could be obtained over a period of a month or more. Initially, this was attempted using SEA2 injection alone at injection rates of 60–100 ppm. The mercury removal rates for the extended period are shown in Figure 21. It is noted that removal as high as 75% was achieved during the first portion of the long-term testing, but only at SEA2 injection rates greater than 100 ppm. It was then determined that SEA2 injected at these rates, along with a small quantity (0.15 lb/Macf) of PAC, was required to meet the target of 55% mercury removal. As previously noted, the injection of SEA2 or SEA2 and PAC precludes obtaining a baseline value while the injections are under way. The percentage of mercury removal for the extended testing is based

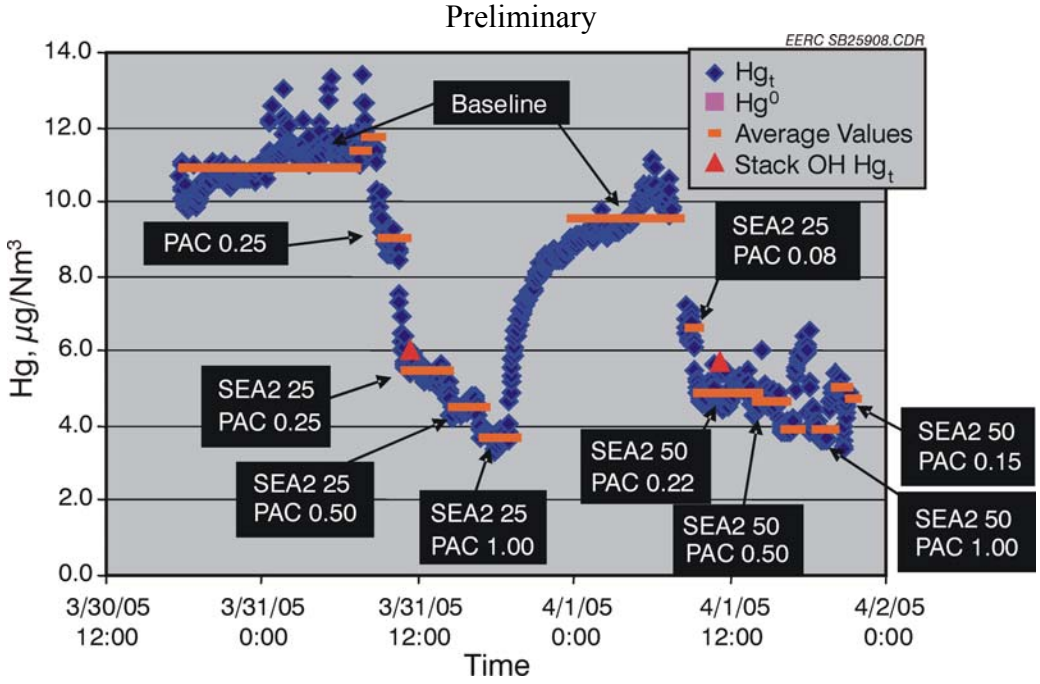

Figure 20. Mercury stack measurements conducted during injection of SEA2 and PAC.

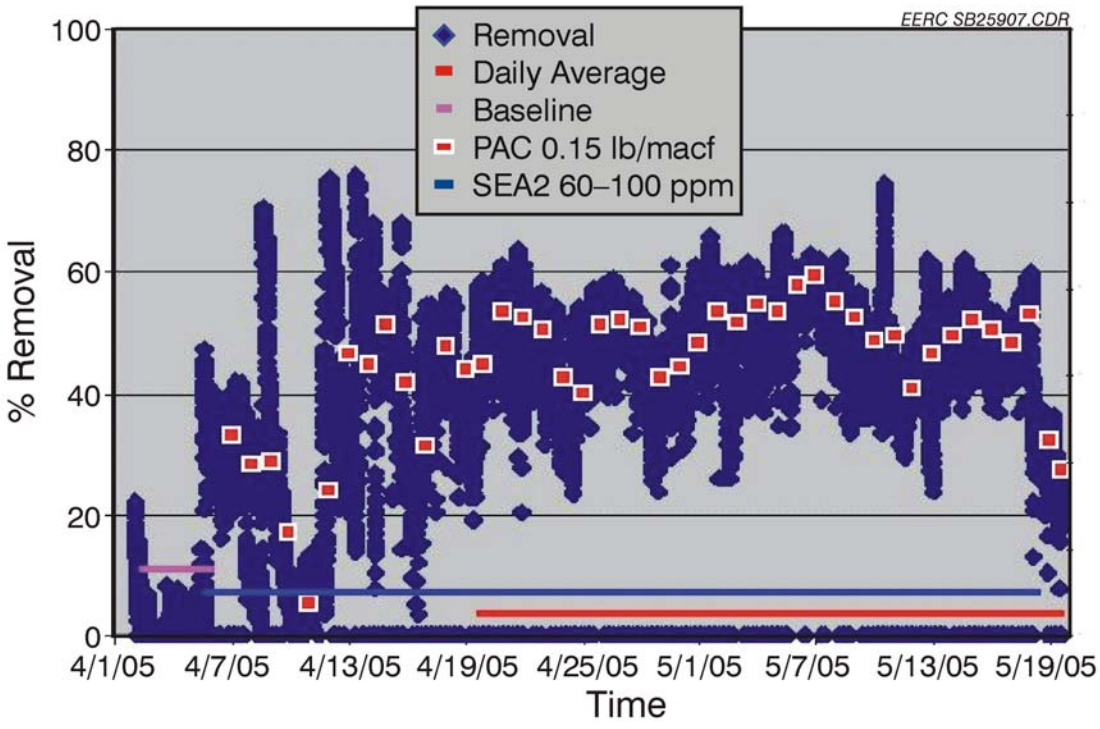

Figure 21. Mercury removal for extended testing at MRY using SEA2 and SEA2 with PAC.

on stack CMM measurements along with stack baseline measurements taken between the completion of the parametric testing and the start of the extended testing. Analyses of coal samples taken during the extended testing period will provide additional information on any variability in mercury concentration when completed. It should also be noted that the delivered cost of concentrated SEA2 increased significantly from when the testing was proposed. This, combined with the higher-than-expected injection rate required, meant that the SEA2 injection rate be the minimum necessary to achieve an estimated 55% mercury removal. This left little margin in case of changes in coal mercury level or fluctuations in pumping rate.

Testing of SEA2 only began April 5 and continued to April 19, 2005. During this period, problems were encountered with stratification of the diluted SEA2 solutions (a concentrated 50 wt/wt% SEA2 aqueous solution was diluted to a nominal 15 wt/wt% solution for injection). This dilution was a necessary consequence of the minimum pump capacity and the pump range. Further problems were experienced because of the quality of the delivered SEA2 solution, which was found to contain small quantities of oil, sludge, and organic debris. Significant scale formation was also encountered over the extended testing period, resulting in the plugging of filters, pumps, and flowmeters. For the SEA2-only portion of the testing, this resulted in erratic SEA injection and consequent fluctuations in the amount of mercury removed. Air agitation of the dilute SEA solution for 3 to 4 hours resulted well-mixed solutions, but sludge and scale formation were a recurring problem. Analysis of the scale has not been performed, but it is expected to show the scale to be common insoluble sulfates.

Injection of SEA2 in combination with a nominal 0.15-lb/Macf PAC injection was initiated April 19 and continued until May 18, 2005, when the supply of SEA2 was exhausted. PAC injection continued for several hours on May 19 after the SEA2 ran out in order to empty the PAC Super Sack feeding the PortaPac injection system.

During the SEA2-PAC injection, the 55% mercury removal target was exceeded 25% of the time, with removal rates as high as 65%; 50% of the time, the removal rate was between 50% and 55%.

4.2.7 Corrosion Probe Characterization – Conducted During This Quarter

4.2.7.1 Introduction

To assess the BOP effects halogen-containing oxidation agents for mercury capture, six air-cooled corrosion test probes were installed at MRY. The probes were installed at the exit of the economizer (ECM), the air heater inlet (AHI), and the air heater outlet (AHO).

4.2.7.2 Probe Design

No standard test method was found in the literature appropriate for corrosion testing of tubing samples in a full-scale utility boiler environment; therefore, a customized testing procedure was developed. Each corrosion probe was designed to hold an 18-in.-long, 1-in.-diameter coupon consisting of a section of boiler tubing. To induce stress in the metal, the tubing is flattened in a 2-in. section at the midpoint to produce an oval with a minimum inside diameter of 0.5 in. The purpose of the flattening is to introduce stress in the metal to enhance potential corrosion.

The coupons are stainless steel. Two coupons for each location were fabricated by MRY personnel: a baseline coupon exposed to the normal flue gas environment and a test coupon exposed to flue gas while oxidation agents are being injected with the coal feed. Actual coupon outside diameter was 1 11/16 in. with a 0.25-in. wall. Reducing couplings were used to join the coupons to the probes.

The corrosion probe assembly is illustrated in Figure 22, and a picture of the coupon and cross-sectioned coupon is shown in Figure 23. The probe is inserted into the boiler through a 4-in. threaded pipe stub attached to the boiler wall. The threaded 4-in. pipe cap supports the probe. Welded to and extending through the pipe cap is a section of 1-in. Schedule 40 pipe. Stainless steel pipe was used for all of the probes. Additional couplings and 18-in. pipe lengths are screwed on to extend the probe length, with the test coupon held at the end. The test coupons are threaded for attachment to the corrosion probe assembly and for a pipe cap to seal the opposite end. A 0.5-in. 316 stainless steel tube runs the length of the probe. Compressed air for cooling is introduced through a pipe tee and flows down the annulus between tubing and probe pipe and back out the stainless steel tubing. A gate valve at the inlet is used to regulate the air flow, and a ball valve provides on/off control. Skin temperatures of the coupons are monitored

Figure 22. Picture of corrosion probe assembly.

Figure 23. Picture of coupon and cross-sectioned coupon.

with a thermocouple extending down the stainless steel tube and pressing against the end cap. A second thermocouple monitors exit cooling air temperature.

4.2.7.3 Coupon Testing

Baseline coupons were exposed to flue gas for 8 weeks, and long-term coupons were exposed to flue gas for 6 weeks, after which they were removed for analysis. On installation, uncooled coupon skin temperature was approximately 800°F at the ECM and 774°F at the AHI. Cooling airflow for the ECM coupon was set to maintain the coupon skin temperature at approximately 461°F, the AHI coupon were set to maintain the coupon skin temperature at approximately 485°F, and the AHO coupon temperature at approximately 272°F. Temperatures were logged with a computer at 5-minute intervals over the duration of the coupon testing. Note

that no feedback control of airflow based on temperature is used, so probe temperatures fluctuated somewhat based on flue gas temperature.

The baseline coupons were in the boiler from 11/18/04 with temperature data obtained from 16:34 to 1/17/05 with data collection ending at 13:12. The temperature profiles for the probes are shown in Figures 24–26. A summary of the temperature data for the baseline coupon testing is given in Table 1. Some temperature information was not obtained as a result of data "dropout" associated with the data logger, but was obtained each hour. During the period of 11/22/04 10:43 to 11/24/04 12:08, the compressed air supply to the AHO probe appears to have been reduced or interrupted, since the probe skin temperature was abnormally higher, and the exit cooling air temperature much lower than for the rest of the test period. At three brief periods between 11/30/04 and 12/13/04, both the probe skin temperature and exiting cooling air temperature went much lower than normal and the probe skin temperature was close to the temperature of its cooling air, indicating either reduced/interrupted flue gas or excess cooling air to the ECM and AH probes in these periods.

The long-term test coupons were tested from 4/5/05 to 5/17/05. However, most of the probe temperature data were lost as a result of computer hard disk failure. The temperature data were retained only for the period of 4/11/05 7:03 to 4/15/05 5:19. The probe temperature profiles of this period are shown in Figures 27–29. A summary of the temperature data for this period of testing is given in Table 2. The probe temperatures in this short period were fairly stable.

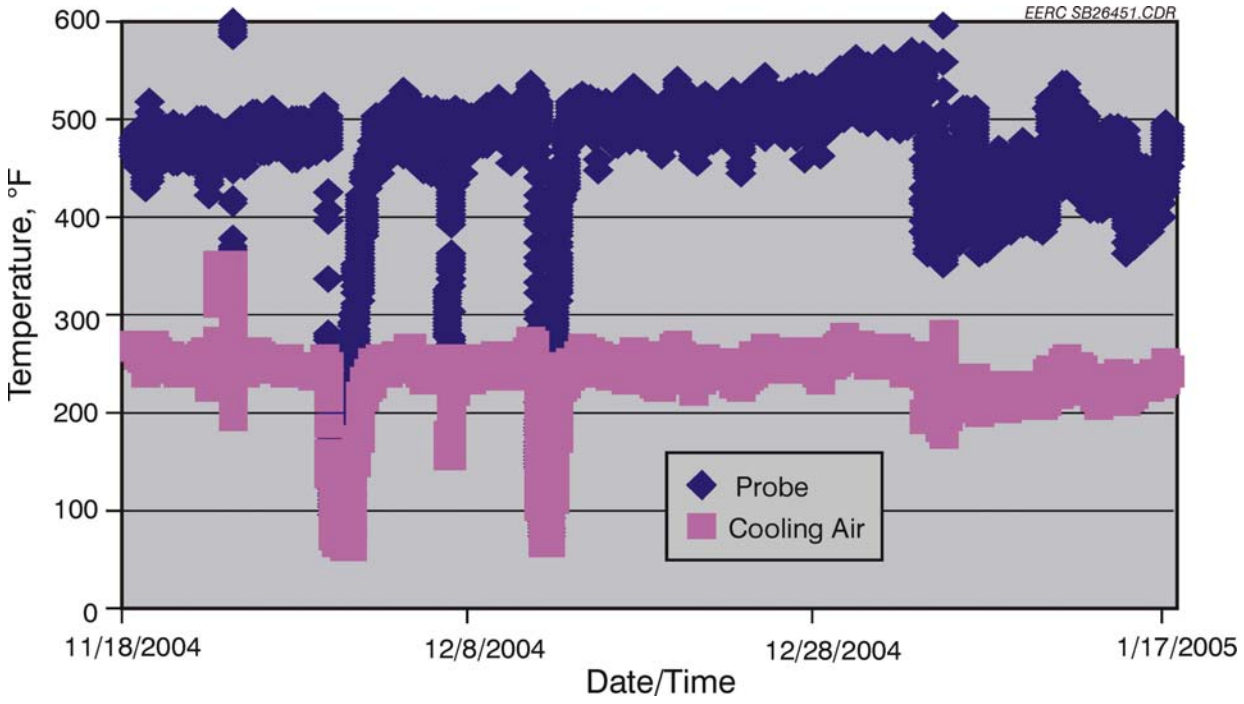

Figure 24. MRY ECM baseline probe temperature profile.

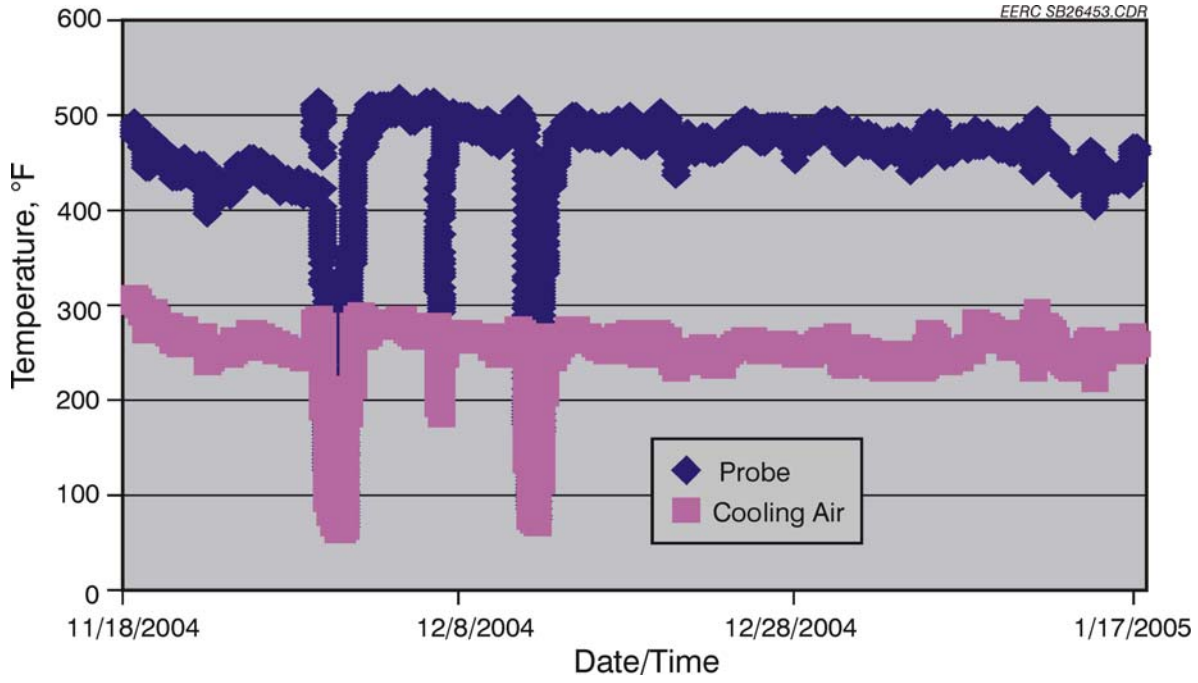

Figure 25. MRY AHI baseline probe temperature profile.

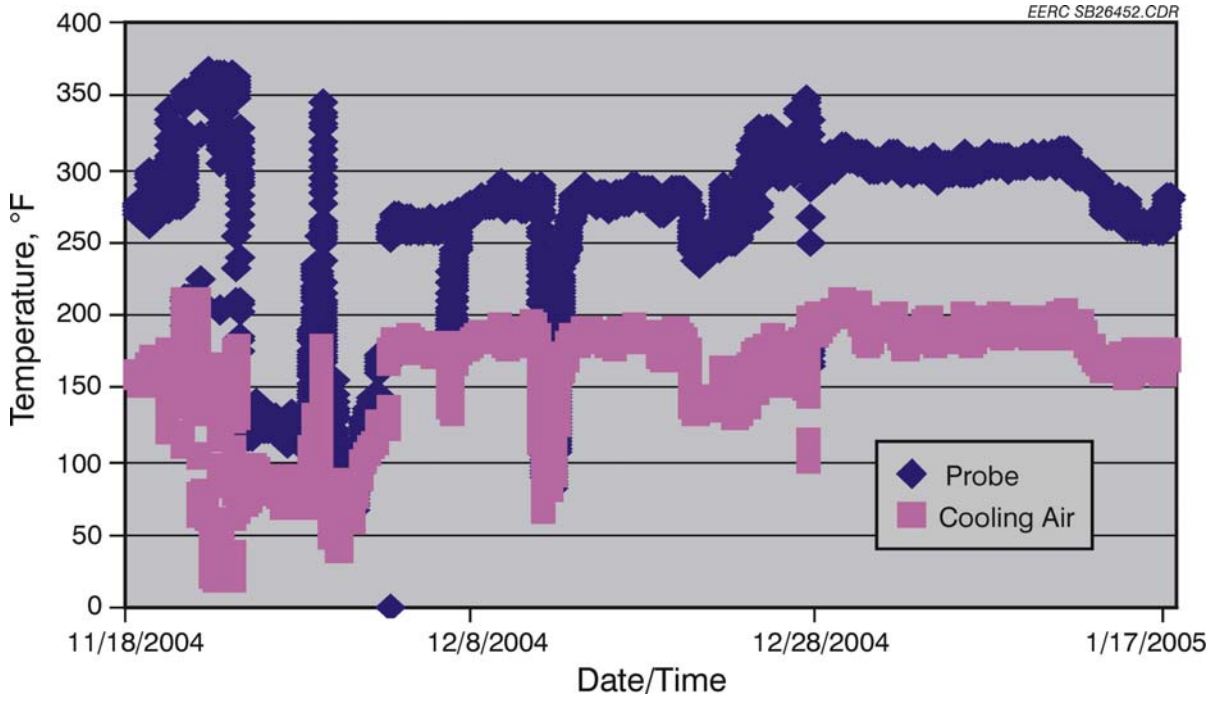

Figure 26. MRY AHO baseline probe temperature profile.

Table 1. Baseline Probe Temperature, °F

	ECM Probe	ECM Cooling Air	AHI Probe	AHI Cooling Air	AHO Probe	AHO Cooling Air
Av	472.2	235.3	453.3	250.0	260.9	158.0
Min.	66.4	58.7	66.6	59.1	55.1	16.3
Max.	878.3	353.3	517.5	307.7	368.7	209.8
Std. Dev.	97.6	38.2	73.4	35.5	65.9	44.3

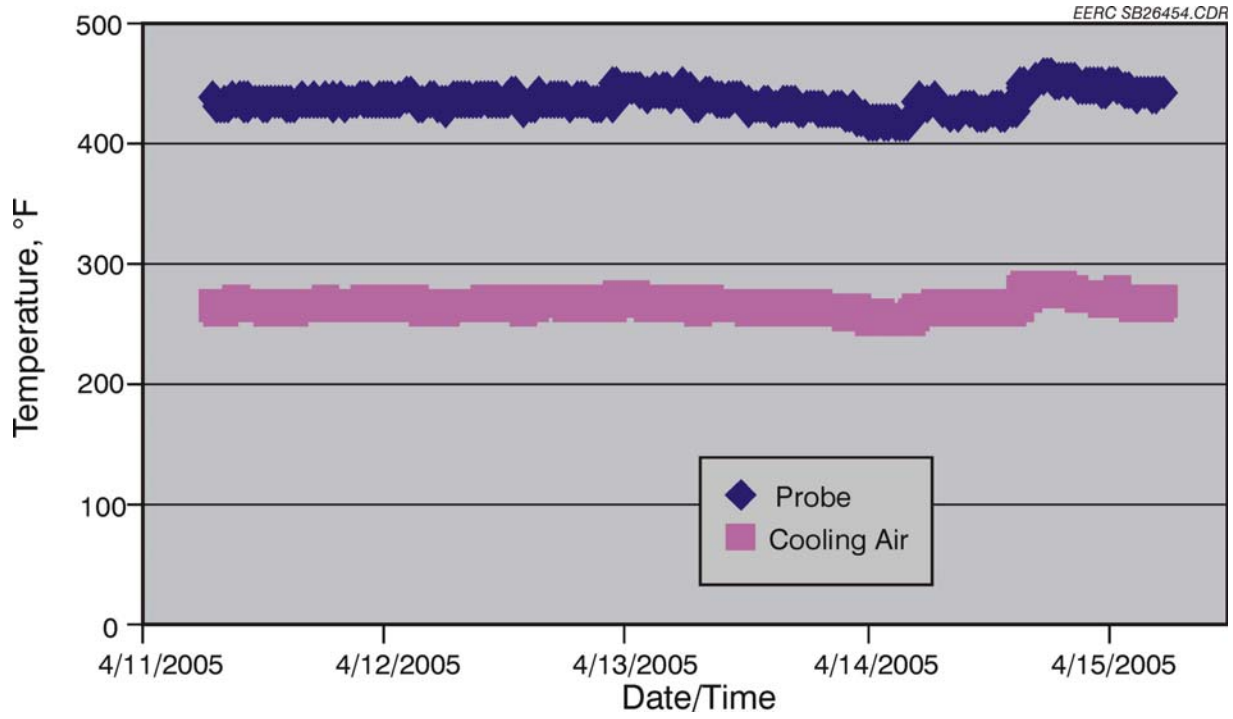

Figure 27. MRY ECM long-term probe temperature profile.

4.2.7.4 Coupon Analysis

To preserve any ash deposit adhering to the probes, they were wrapped in plastic film and placed in cardboard tubes prior to transport. Upon arrival at the EERC, the test coupon sections of the probes were sprayed with a mixture of acetone and epoxy to affix the ash deposits during subsequent cutting. The test coupons were cross-sectioned with a metal band saw at the midpoint of the crimped area. The cutting operation was performed without lubrication to prevent contamination of the coupons. The samples were then mounted in epoxy and polished to obtain samples for scanning electron microscopy (SEM) analysis.

All of the six coupon samples were examined by SEM to ascertain the degree of corrosion at the metal–metal oxide–deposit interface. Line scans were performed for each sample on one of the curved sections and one of the flat sections. Four lines were selected at each location for

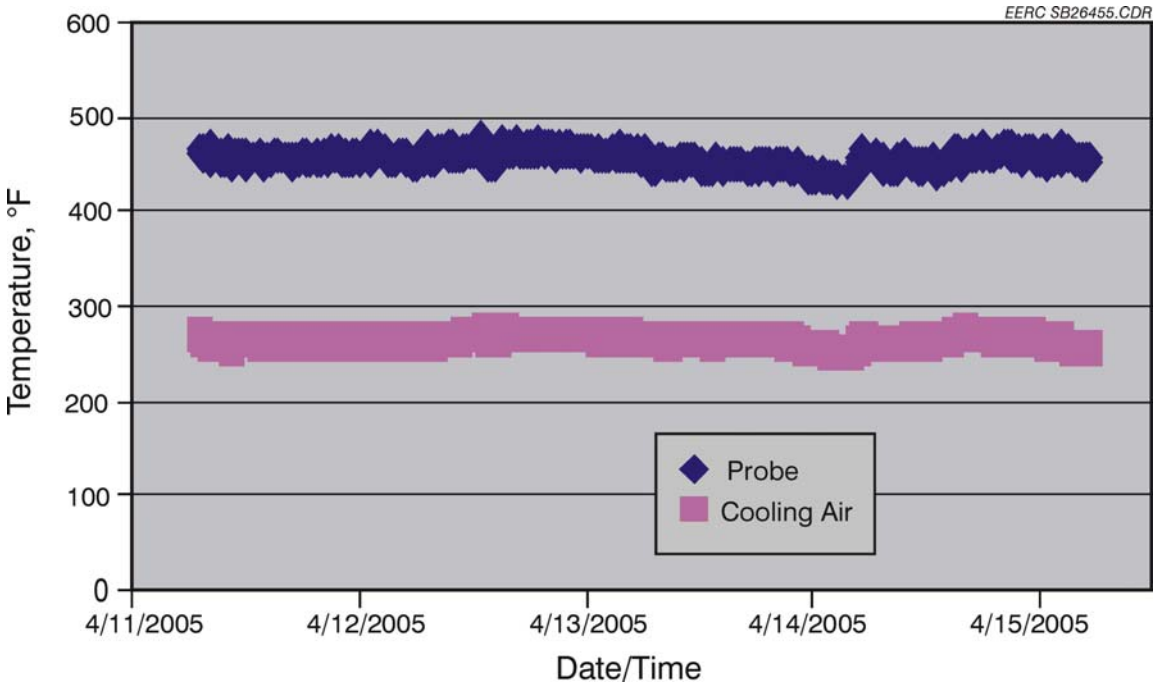

Figure 28. MRY AHI long-term probe temperature profile.

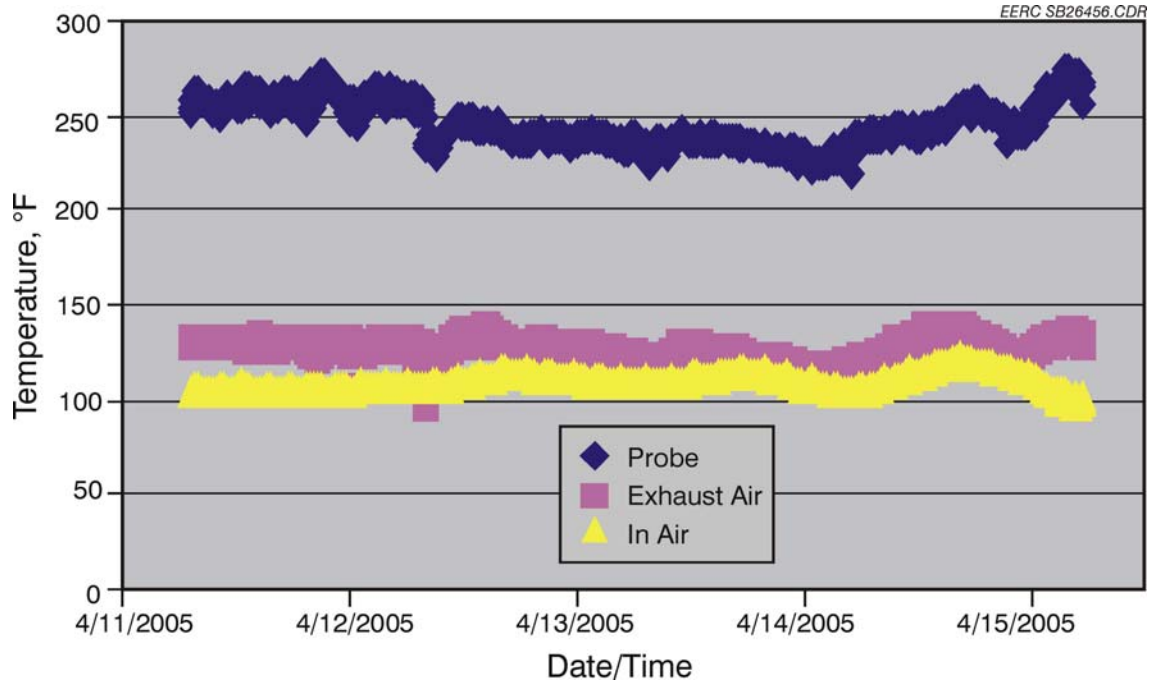

Figure 29. MRY AHO long-term probe temperature profile.

Table 2 . Long-Term Probe Temperature, °F

	ECM Probe	ECM in Air	AHI Probe	AHI Exh. Air	AHO Probe	AHO Exh. Air	AHO in Air
Av	435.7	266.1	456.0	264.4	245.3	127.2	109.0
Min.	414.3	252.7	430.7	250.0	220.1	97.4	97.5
Max.	457.0	281.2	478.7	276.8	274.6	138.9	121.3
Std. Dev.	8.1	4.9	8.2	4.7	11.5	5.0	4.2

quantitative point analyses for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Fe, Ni, Mn, and O. Each line covers 40 μm long across the metal–metal oxide–deposit interface, and 81 point analyses were done along the line in equal intervals between points.

4.2.7.4.1 Economizer Coupons

Figure 30 shows the appearance of typical areas of the steel–oxide interface for the curve and flat sections of the ECM baseline and long-term coupons. The bright area at the right of each picture is the steel; the gray area is the surface oxide layer, and the black area at the left is the epoxy in which the coupon section is mounted. For both the baseline and long-term samples, a portion of the deposit is seen as closely packed gray spheres at the left of the pictures. The baseline coupon sample has a smooth steel surface, while the long-term test coupon sample has a rough steel surface, indicating more extensive corrosion of the long-term test coupons. On the flat section, the baseline sample shows a thicker layer of deposit than the long-term sample.

Figures 31 and 32 give typical results of SEM line scan analyses for iron, chrome, nickel, sulfur, sodium, potassium, calcium, silicon, and aluminum for the economizer coupons. Some analysis points outside of the iron oxide interface and deposit layer reported high chlorine contents. This is caused by the sample-mounting material, which is chlorine-based epoxy. Results of the four line scans on each of the curve and flat sections of the economizer coupons are very similar, and two sets of baseline and long-term testing are presented in the plots.

The line scans show a decrease in iron content going from the tube metal to the oxide layer. The deposits also show significant iron content resulting from iron-rich fly ash particles. Both the baseline and long-term coupons have high levels of sulfur in the oxide and deposit layers. On the flat section, the deposits on the long-term coupon have much higher sulfur content than the deposits on the baseline coupon. On the curve section, the sulfur contents in the deposits on the baseline and long-term coupons are not significantly different. It seems that sulfur is the primary oxidation agent causing the coupon corrosion.

Aluminum, silicon, and calcium are the major elements comprising the deposits on the coupons. The deposits on the baseline coupon have relatively higher aluminum and silicon contents than the deposits on long-term coupons, while the deposits on the long-term coupon have much higher calcium content than the deposits on baseline coupons, especially on the curve section. This suggests that some increase in calcium sulfate deposition is occurring as a result of the SEA2 addition in long-term test.

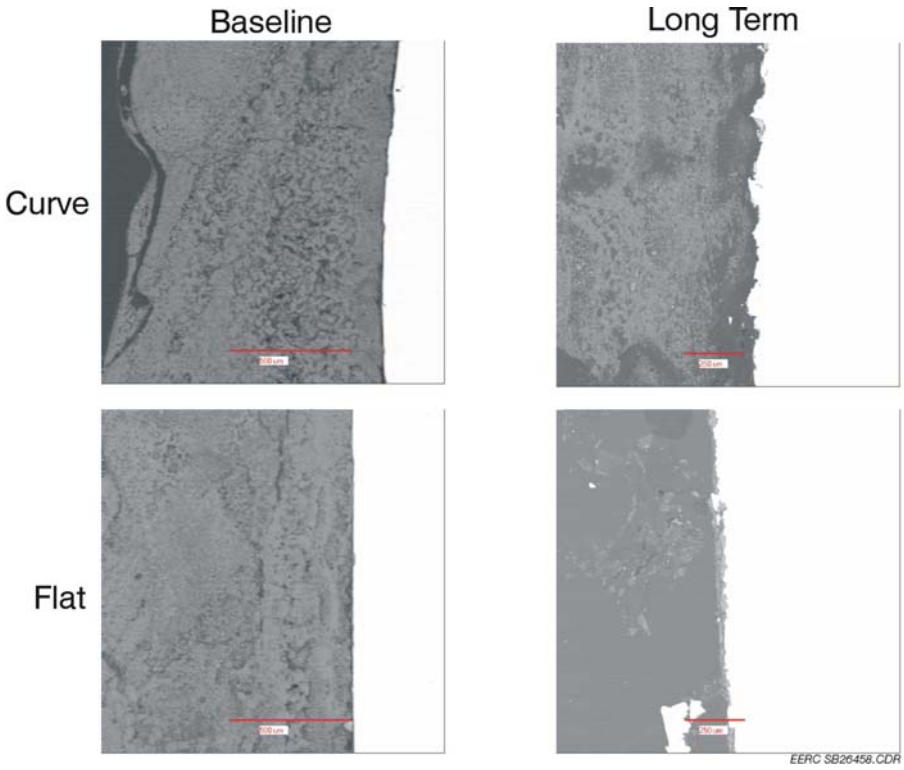

Figure 30. Backscattered electron image of MRY ECM coupons.

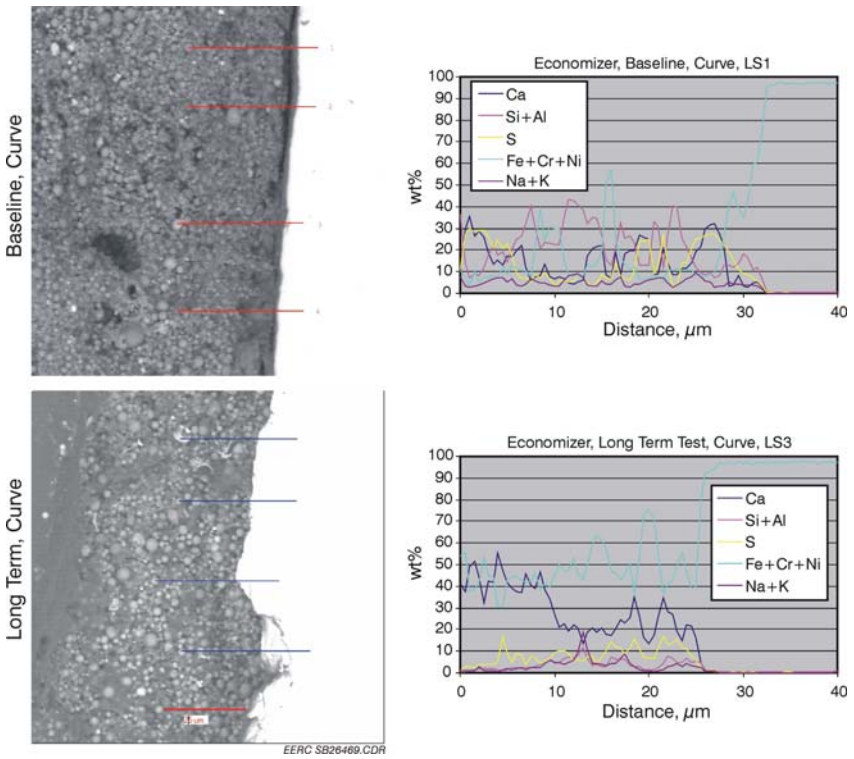

Figure 31. Comparison of ECM baseline and long-term coupons.

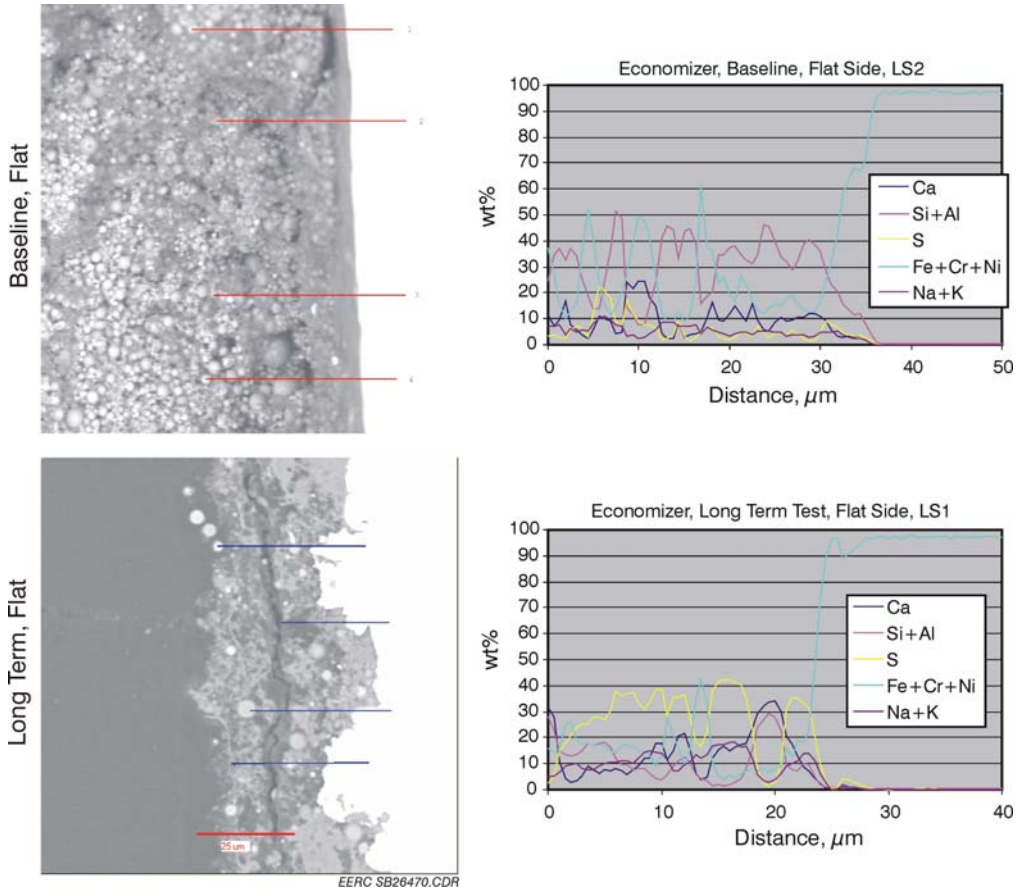

Figure 32. Comparison of ECM baseline and long-term coupons.

4.2.7.4.2 AHI Coupons

Figure 33 shows the appearance of typical areas of the steel–oxide interface for the AHI baseline and long-term coupons. The bright area at the right of each picture is the steel, the gray area is the surface oxide layer, and the black area at the left being the epoxy in which the coupon section is mounted. Note that the photographs of the AHI coupons are similar to that of the economizer coupons shown in Figure 30, the baseline coupons have a smooth steel surface, and the long-term coupons have a rough steel surface, indicating more intensive corrosion of long-term coupons. The deposit layers, however, are much thinner than that of economizer coupons. The long-term deposits are closely packed on the steel surface, while there is a "crack" between the deposit layer and the steel surface on baseline coupons.

The results of SEM line scan analysis giving Fe, Cr, Ni, S, Na, K, Ca, Al and Si concentrations for the AHI coupons are shown in Figures 34 and 35. In general, these results are similar to those seen for the ECM coupons. A notable difference is that the deposits on long-term coupons have much higher Na, K, and S concentrations. On the flat section of the long-term coupon, the deposit layer is composed of pure Na, K, and Ca sulfates, without aluminosilicate fly ash and iron-rich particles. The total Na and K concentration is as high as over 40% in some

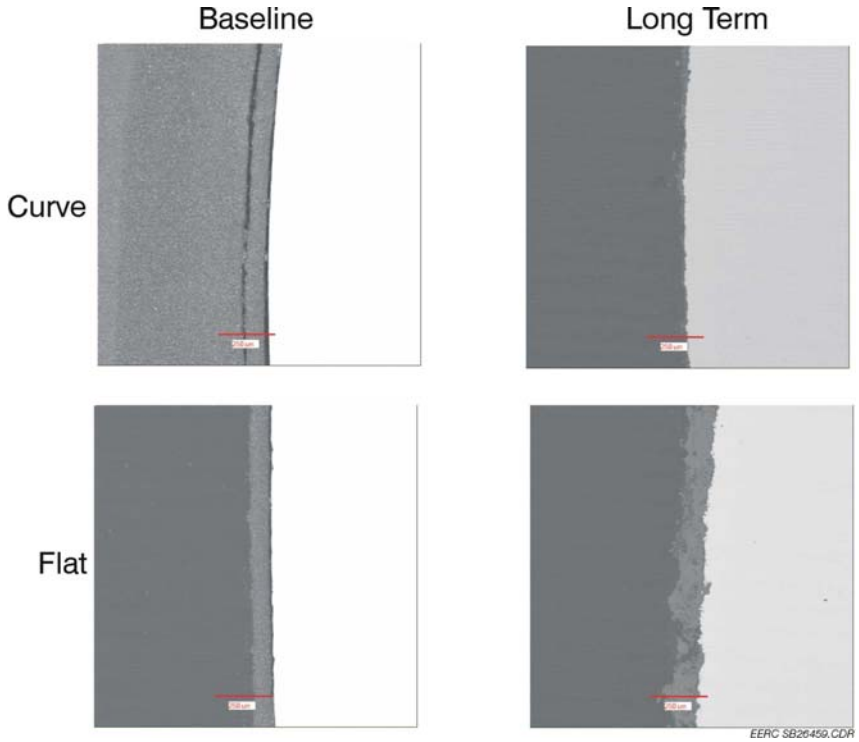

Figure 33. MRY AHI coupons.

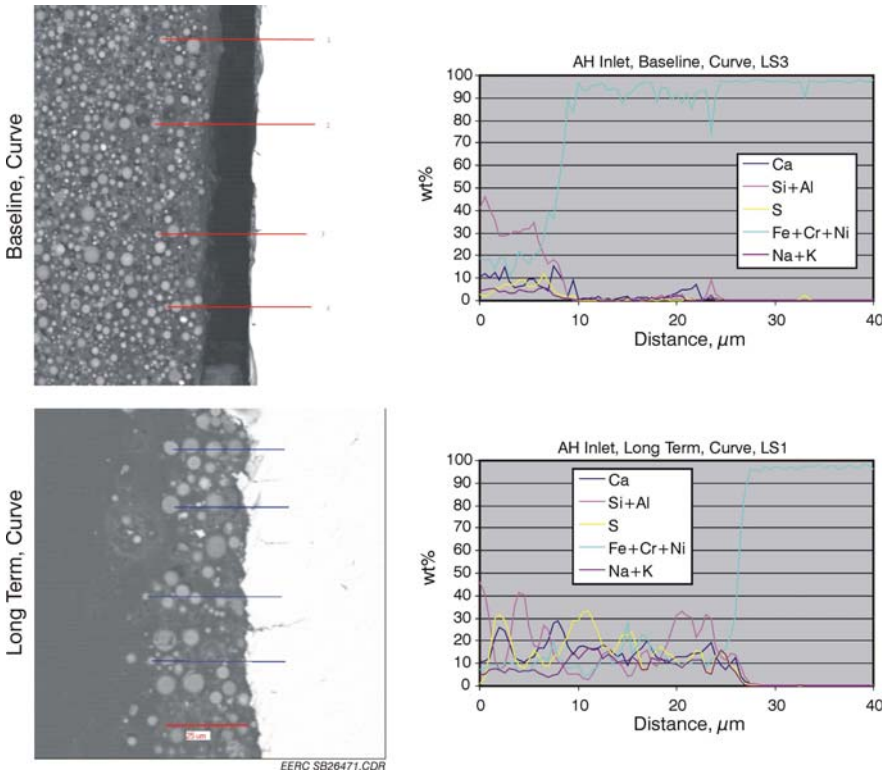

Figure 34. Comparison of AHI baseline and long-term coupons (curved side).

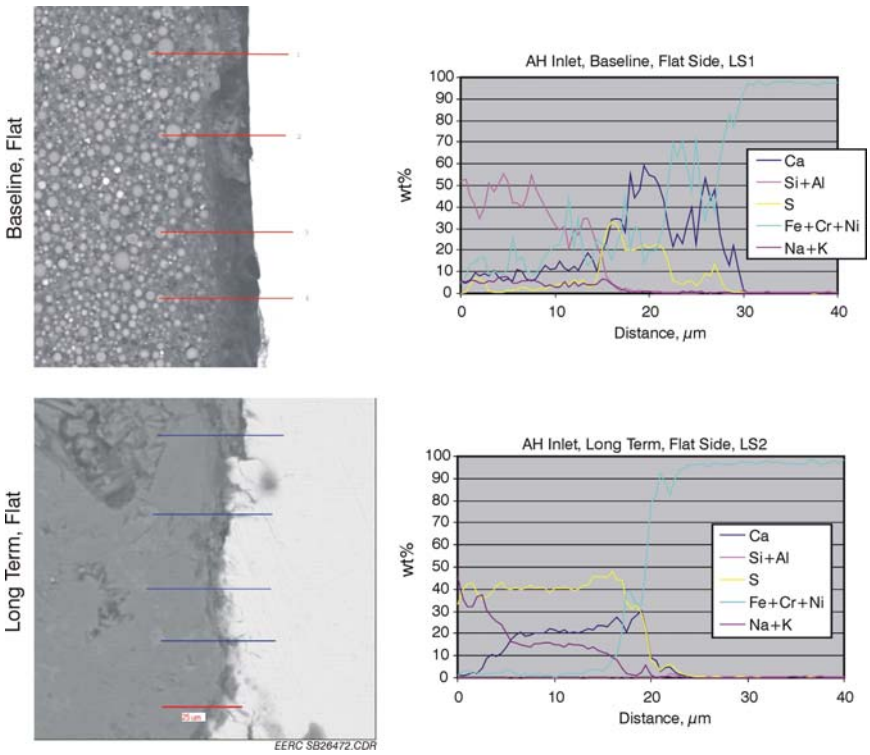

Figure 35. Comparison of AHI baseline and long-term coupons (flat side).

parts of the deposit layer. The analysis results do not clearly show increased Ca concentration in the long-term deposit layer.

4.2.7.4.3 AHO Coupons

Figure 36 shows the appearance of typical areas of the steel–oxide interface for the AHO baseline and long-term coupons. The bright area at the right of each picture is the steel, the gray area is the deposit layer, and the black area at the left being the epoxy in which the coupon section is mounted. The deposit layer on the baseline coupon is much thicker than that of the long-term coupon. Unlike the ECM and AHI coupons, the steel surfaces the AHO baseline and long-term coupons look similar. The long-term coupon steel surface is not as rough as that of the ECM and AHI long-term coupons. There is no indication of more intensive corrosion of the long-term coupon than the baseline coupon.

The results of SEM line scan analyses giving Fe, Cr, Ni, S, Na, K, Ca, Al, and Si concentrations for the AHO coupons along with the micrographs of the scanned area are shown in Figures 37 and 38. It is interesting that the deposit layer on the curve is different from that on the flat section of the same coupon. On the baseline coupon, although both the curve and flat sections have a deposit layer of aluminosilicate fly ash particles cemented by Na, K, and Ca sulfates, the fly ash particles at the curve are submicrometer to about 2 μm in diameter, while the particles at the flat sections are much coarser, up to over 30 μm in diameter. On the long-term coupon, the deposit layer of the flat section is composed of fine aluminosilicate particles

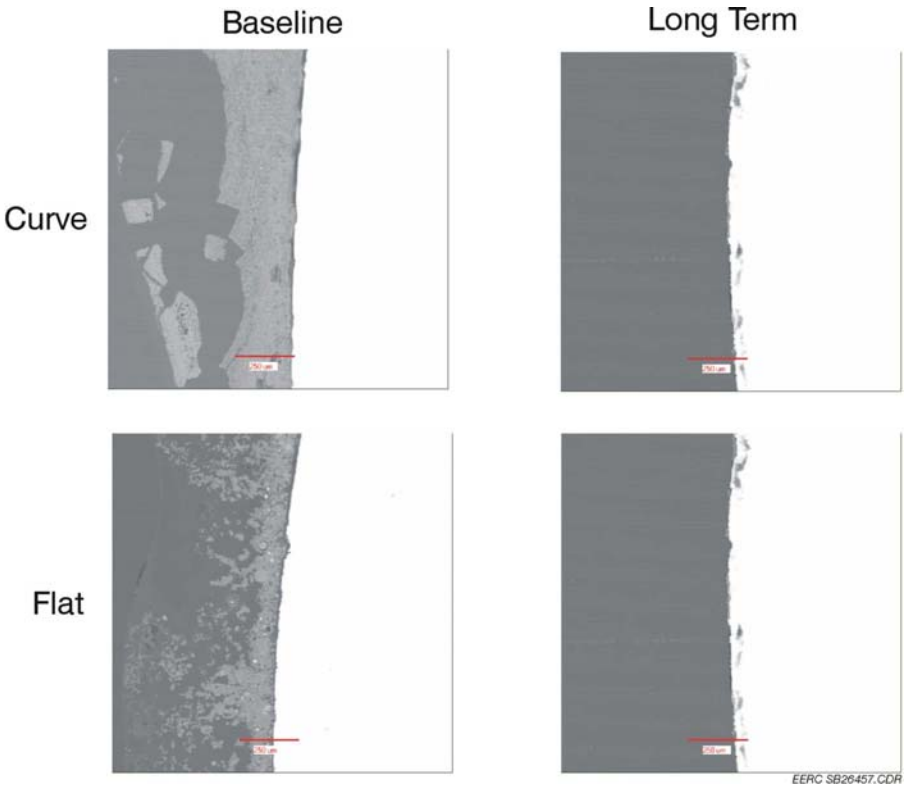

Figure 36. MRY AHO coupons.

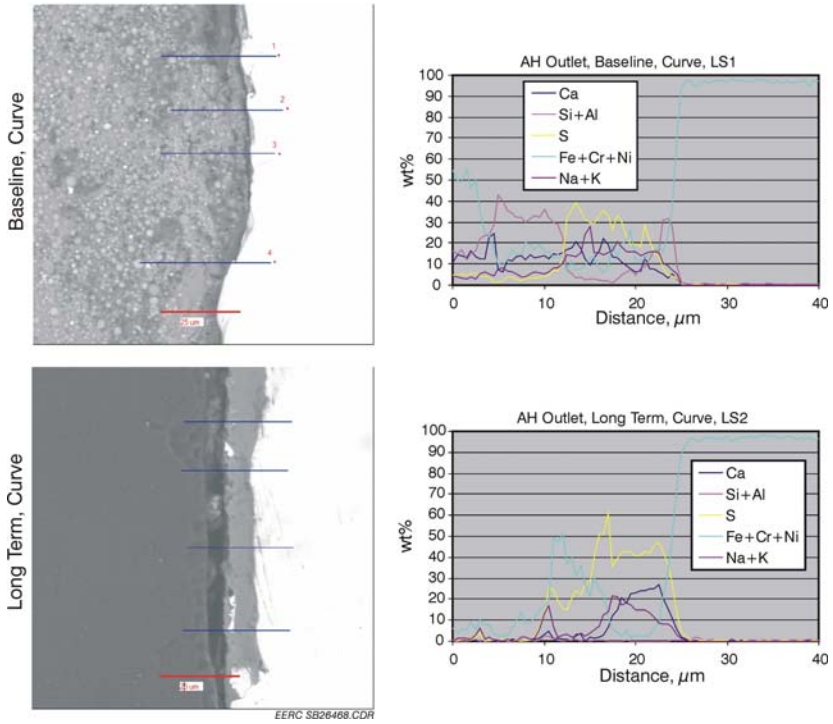

Figure 37. Comparison of AHO baseline and long-term coupons.

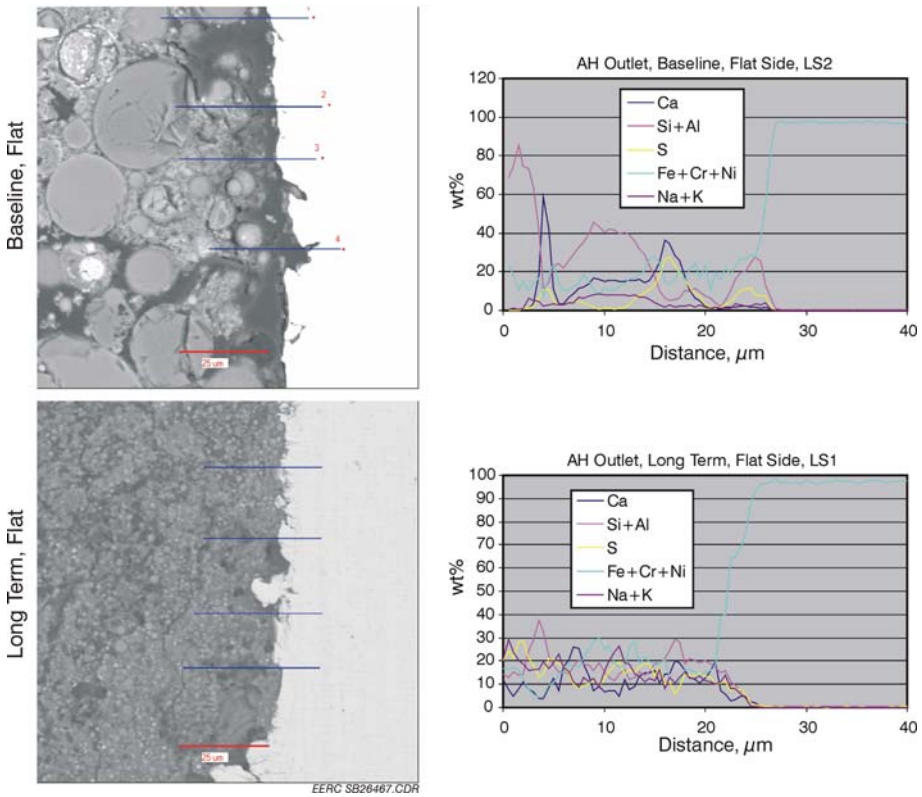

Figure 38. Comparison of AHO baseline and long-term coupons.

cemented with Na, K, and Ca silicate, while the deposit on the curve is a thin layer of Na, K, and Ca sulfates, without aluminosilicate particles found.

Chemically, these results are similar to those seen for the ECM and AHI coupons. The long-term deposit has higher Na, K, and S concentrations and lower Al and Si concentrations than the baseline deposit. On the curve, the long-term coupon has higher Ca in the deposit layer than the baseline coupon, while on the flat section, this phenomenon is not well held. It is hard to conclude that expositing SEA2 has increased Ca sulfate deposition on the long-term coupon.

4.3 Results from Monticello Testing

No data were generated for this quarter.

5.0 CONCLUSIONS AND PLANNED ACTIVITIES FOR NEXT QUARTER

5.1 Task 1 – MRY Testing

Overall Conclusions

- The parametric testing was nearly completed this quarter. The preliminary results of the initial parametric testing indicated that SEA1 did not show the level of oxidation necessary to achieve the 55% level of control. SEA2 showed much higher removal rates than SEA1. The addition of small amounts of carbon enhanced the removal of mercury across the ESP and FGD. The removal is taking place in the ESP and not in the FGD.

- Longer-term testing (1 to 2 months) of chemical addition was conducted to enhance Hg oxidation and capture in the ESP and wet FGD at the MRY plant. Initial testing of SEA2 injection alone at injection rates of 60–100 ppm was conducted. Removal rates of mercury were found to be as high as 75%, but only at SEA2 injection rates greater than 100 ppm. The quantity of SEA2 required was above the level anticipated based on pilot-scale studies. The effectiveness of the SEA2 may have been diminished because of the high sodium and calcium contents of the lignite fired.

- Longer-term testing was continued by injecting SEA2 at about 60 ppm along with a small quantity (0.15 lb/Macf) of PAC which was required to meet the target of 55% mercury removal. Injection of SEA2 in combination with a nominal 0.15-lb/Macf PAC injection initiated April 19 and continuing until May 18, 2005, when the supply of SEA2 was exhausted. PAC injection continued for several hours on May 19 after the SEA2 ran out in order to empty the PAC Super Sack feeding the PortaPac injection system. During the SEA2 PAC injection, the 55% mercury removal target was exceeded 25% of the time, with removal rates as high as 65%; 50% of the time, the removal rate was between 50% and 55%.

Conclusions for This Quarter

- Corrosion probes were analyzed, and the results indicated that the economizer and AHI long-term test coupons have more rough or cracking metal surfaces, possibly indicating more corrosion as a result of being exposed to the SEA2 additive. The deposit layers of ECM, AHI, and AHO long-term coupons have more or less higher S, Ca, Na, and K concentrations, indicating possible alteration of deposit chemistry caused by exposure to SEA2. In summary, the SEA2 addition may have caused more corrosion of the ECM and AHI long-term coupons. Longer tests and further investigation are necessary to confirm the effect of SEA2 on steel corrosion. The increase in corrosion may also be due to changes in coal quality between baseline and long-term testing. Analysis of the coal properties will be conducted next quarter to determine if coal properties contributed to the changes in deposition behavior and corrosion potential.

Planned Activities

- Sample analysis and data interpretation will be continued during the next quarter.

5.2 Task 2 – Monticello Testing

Conclusions for This Quarter

Full-scale tests were initiated at Monticello Unit 3 (fall 2005) to evaluate the effectiveness of chemical addition on Hg control across an ESP wet scrubber configuration.

Planned Activities

- Testing will be completed next quarter and sample analysis and data interpretation will be initiated.

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